

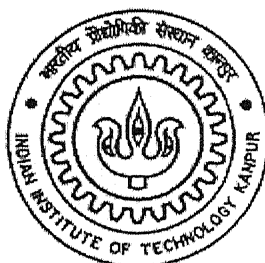
# COMPUTATION OF LLE AND EVALUATION OF SOLVENTS FOR AROMATIC EXTRACTION

*A Thesis submitted  
in partial fulfilment of the requirements  
for the Degree of*

*Master of Technology*

*by*

**Rajbahadur Singh Tanwar**



*to the*

**Department of Chemical Engineering**

**INDIAN INSTITUTE OF TECHNOLOGY, KANPUR**

February 2001

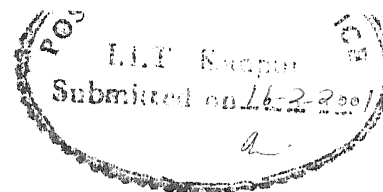
16 APR 2001 / CHE  
के प्रो. प्रतिलिपि  
प्रो. प्रो. प्रो. प्रो.  
अवधि-०० A133695

TH  
CHE/2001/01  
T159c



A133695

# CERTIFICATE



This is to certify that the work contained in the thesis entitled "**COMPUTATION OF LLE AND EVALUATION OF SOLVENTS FOR AROMATIC EXTRACTION**" has been carried out by *Rajbahadur Singh Tanwar* under my supervision and that it has not been submitted elsewhere for a degree.

February 2001

*Ashok Khanna*

**Dr. Ashok Khanna**

Professor,

Dept. of Chemical Engineering,

Indian Institute of Technology,

Kanpur – 208 016, India

## ABSTRACT

The extraction of Aromatics from petroleum naphtha is an important commercial operation. Because of increasing cost of energy and ever-increasing need for pure aromatic hydrocarbons, the efficient purification and separation of aromatics is considered essential for modern refineries. The solvents used for extraction of aromatics now a day's either have good selectivity with simultaneously low solvent capacity or vice versa. Therefore it is valuable to search for new solvents, and to estimate the performance of existing solvents.

The selectivity and solvent capacity are the two primary parameters used for comparison of solvents. A performance index based on the above two parameters has been used to categorize the solvents for aromatic extraction. The selectivity and solvent capacity are generally estimated using activity coefficient models. These models require proper binary interaction parameters for accurate representation of LLE. These parameters are not yet available for all aromatic extraction systems. Furthermore the parameters available for almost all the systems are found to be specific to that system, and can not be used outside that system. For estimation of parameters for thermodynamic models such as UNIQUAC and UNIFAC the ternary LLE data have been used. The parameter estimation procedure used here has been modified to estimate the parameters simultaneously for different systems involving common pairs. The regressed parameters using this technique have been shown to be applicable for other ternary and multi-component systems. The regressed parameters then have been used to estimate the performance of different solvents for aromatic extraction

## Acknowledgements

To my thesis supervisor Dr. Ashok Khanna, for the valuable advice and encouragement that I got from him throughout. My gratitude to him is immense and cannot really be expressed in words. I consider it a rare privilege that I could work under him.

To all the professors of the department who showed the rigors and beauties of Chemical Engineering and encouraged me in all ways.

I would like to thank ‘Deba and Tapan’ for giving me a wonderful company. The wonderful time I had here with my lab mates will be remembered, forever.

To all my friends – within and outside IIT.

To IITK itself, for its stimulating academic environment. And also for gifting me with many special moments.

Financial support from BPCL project entitled “Extraction of Aromatics from Petroleum Naphtha” is gratefully acknowledged.

# CONTENTS

<b>List of Figures</b>	<b>ix</b>
<b>List of Tables</b>	<b>xi</b>
<b>Nomenclature</b>	<b>xiv</b>

## Chapter

<b>1</b>	<b>Introduction</b>	<b>1</b>
<b>2</b>	<b>Literature Review</b>	<b>5</b>
	➤ Solvent Selection Strategies	5
	• Limiting activity coefficients	5
	• Industrially used aromatic extraction processes	5
	• Molecular Design of Solvents	8
	➤ Parameter Estimation	8
<b>3</b>	<b>Solvent selection strategies</b>	<b>11</b>
	➤ Important characteristics of solvents for aromatic extraction	11
	• Solvent Selectivity	12
	• Solvent Capacity	12
	➤ Search for new solvents	13
	• Molecular Design of Solvents	13
	(a) Classification of groups	13

	(b) Selection of groups and target properties	14
	(c) Formation of feasible chemical compounds (combination rules)	15
	(d) Evaluation of solvent properties and screening of compounds	15
	➤ Screening of Solvents based on Infinite Dilution Activity Coefficients	16
	• Selectivity at infinite dilution of solutes	16
	• Solvent capacity at infinite dilution of solute	17
	• Performance Index at infinite dilution of solute	17
	➤ List of potential solvents and screening	17
<b>4</b>	<b>Parameter Estimation</b>	<b>22</b>
	➤ Least square minimization	23
	➤ Maximum likelihood estimation	25
	• Maximum likelihood principle	25
	• Maximum likelihood estimation	26
	➤ Algorithm for parameter estimation using LLE data	28
<b>5</b>	<b>Parameter Estimation Results</b>	<b>33</b>
	➤ Separate Estimation of parameters	33
	• Hexane-Benzene-TMS	35
	• Hexane-Benzene-DMSO	35

➤ Simultaneous Estimation of parameters involving common pairs	39
• Systems with TMS	39
• Systems with PC	52
• Systems with N-Formyl-Morpholine	57
• Systems with Dimethyl-Sulfoxide (DMSO)	59
• Systems with Triethylene-Glycol (TREG)	61
• Systems with N-Methyl-Pyrrolidone	61
• Systems with Dimethyl-Formamide (DMF)	62
• System with DEG	64
➤ Effect of Temperature on binary interaction parameters	64
<b>6. Solvent Performance Evaluation Results</b>	<b>70</b>
➤ Interchange Energies	70
➤ Performance of Solvents for a Single Stage Extraction	70
<b>7. Conclusions and Recommendations</b>	<b>81</b>
➤ Conclusions	81
➤ Recommendations	82

<b>References</b>	<b>83</b>
<b>Appendix</b>	
<b>A     Activity Coefficient Models</b>	<b>90</b>
UNIQUEAC Activity coefficient model	90
UNIFAC Activity coefficient model	92
<b>B     Nelder Mead optimisation technique</b>	<b>94</b>
<b>C     Computer Programmes</b>	<b>96</b>

## List of Figures

<b>Figure 3.1</b>	Variation of Selectivity with Temperature	19
<b>Figure 3.2</b>	Variation Solvent Capacity with Temperature	20
<b>Figure 3.3</b>	Variation of Performance Index with Temperature	21
<b>Figure 4.1</b>	Ternary Diagram	30
<b>Figure 5.1</b>	Comparison of LLE Predictions using Separate Estimation with initial guess (1)	36
<b>Figure 5.2</b>	Comparison of LLE Predictions using Separate Estimation with initial guess (2)	37
<b>Figure 5.3</b>	Comparison of LLE Predictions using Simultaneous Estimation	41
<b>Figure 5.4</b>	Comparison of LLE Predictions for Heptane – Xylene – TMS (worst case)	50
<b>Figure 5.5</b>	Comparison of LLE Predictions for Heptane –Toluene–PC	55
<b>Figure 5.6</b>	Temperature Dependence of Parameters for Hexane – Benzene - TMS	66
<b>Figure 5.7</b>	Temperature Dependence of Parameters for Heptane – Toluene - TMS	67
<b>Figure 5.8</b>	Temperature Dependence of Parameters for Cyclohexane – Benzene - TMS	68

<b>Figure 5.9</b>	Temperature Dependence of Parameters for Hexane – Benzene – DMSO	69
<b>Figure 6.1</b>	Variation of Selectivity with % Aromatics in Feed	73
<b>Figure 6.2</b>	Variation of Solvent Capacity with % Aromatics in Feed	74
<b>Figure 6.3</b>	Variation of Performance Index with % Aromatics in Feed	75
<b>Figure 6.4</b>	Variation of Selectivity with Solvent to Feed Ratio	76
<b>Figure 6.5</b>	Variation of Solvent Capacity with Solvent to Feed Ratio	77
<b>Figure 6.6</b>	Variation of Performance Index with Solvent to Feed Ratio	78
<b>Figure 6.7</b>	Variation of Selectivity with Temperature	79
<b>Figure 6.8</b>	Variation of Performance Index with Temperature	80

## List of Tables

<b>Table 2.1</b>	Processes used for extraction of aromatics	7
<b>Table 3.1(a)</b>	Groups identified for aromatic extraction solvents	15
<b>Table 3.1(b)</b>	Performance Index for Solvents along with References	18
<b>Table 5.1(a)</b>	Ternary Systems used for parameter estimation	34
<b>Table 5.1(b)</b>	Multicomponent systems used for comparison	34
<b>Table 5.2</b>	UNIQUAC parameters for System Hexane-Benzene-TMS	38
<b>Table 5.3</b>	UNIQUAC parameters for Hexane-Benzene-DMSO at 298.15 K	38
<b>Table 5.4</b>	Simultaneous UNIQUAC parameters for Hexane-Benzene-TMS, Hexane-Toluene-TMS and Hexane – Xylene – TMS at 298.15 K	40
<b>Table 5.5</b>	UNIFAC group interaction parameters for TMS with other main groups	42
<b>Table 5.6</b>	Comparison of Predictions using UNIFAC with experimental data for the systems Hexane-Benzene-TMS, Hexane-Toluene-TMS and Hexane-Xylene-TMS	42
<b>Table 5.7</b>	Comparison of Predictions using UNIFAC with experimental data for the systems Octane-Benzene-TMS, Octane-Toluene-TMS and Octane-Xylene-TMS	43
<b>Table 5.8</b>	Simultaneous UNIQUAC parameters for Octane-Benzene-TMS, Octane-Toluene-TMS, and Octane-Xylene-TMS at 298.15 K	44
<b>Table 5.9</b>	Comparison of experimental data for quaternary system Hexane(1)-Benzene(2)-Xylene(3)-TMS(4) with UNIQUAC and UNIFAC predictions.	45
<b>Table 5.10</b>	Comparison of experimental data for quaternary system Hexane(1)-Octane(2)-Benzene(3)-TMS(4) with UNIQUAC and UNIFAC predictions.	46
<b>Table 5.11</b>	Comparison of experimental data for quaternary system Octane(1)-Toluene(2)-Xylene(3)-TMS (4) with UNIQUAC and UNIFAC predictions at 298.15 K.	47
<b>Table 5.12</b>	Comparison of experimental data for quinary system Hexane(1) - Octane(2)-Benzene(3)-Toluene(4)-TMS(5)	

## List of Tables

<b>Table 2.1</b>	Processes used for extraction of aromatics	7
<b>Table 3.1</b>	Groups identified for aromatic extraction solvents	15
<b>Table 3.1</b>	Performance Index for Solvents along with References	34
<b>Table 5.1(a)</b>	Ternary Systems used for parameter estimation	36
<b>Table 5.1(b)</b>	Multicomponent systems used for comparison	37
<b>Table 5.2</b>	UNIQUAC parameters for System Hexane-Benzene-TMS	38
<b>Table 5.3</b>	UNIQUAC parameters for Hexane-Benzene-DMSO at 298.15 K	38
<b>Table 5.4</b>	Simultaneous UNIQUAC parameters for Hexane-Benzene-TMS, Hexane-Toluene-TMS and Hexane – Xylene – TMS at 298.15 K	40
<b>Table 5.5</b>	UNIFAC group interaction parameters for TMS with other main groups	42
<b>Table 5.6</b>	Comparison of Predictions using UNIFAC with experimental data for the systems Hexane-Benzene-TMS, Hexane-Toluene-TMS and Hexane-Xylene-TMS	42
<b>Table 5.7</b>	Comparison of Predictions using UNIFAC with experimental data for the systems Octane-Benzene-TMS, Octane-Toluene-TMS and Octane-Xylene-TMS	43
<b>Table 5.8</b>	Simultaneous UNIQUAC parameters for Octane-Benzene-TMS, Octane-Toluene-TMS, and Octane-Xylene-TMS at 298.15 K	44
<b>Table 5.9</b>	Comparison of experimental data for quaternary system Hexane(1)-Benzene(2)-Xylene(3)-TMS(4) with UNIQUAC and UNIFAC predictions.	45
<b>Table 5.10</b>	Comparison of experimental data for quaternary system Hexane(1)-Octane(2)-Benzene(3)-TMS(4) with UNIQUAC and UNIFAC predictions.	46
<b>Table 5.11</b>	Comparison of experimental data for quaternary system Octane(1)-Toluene(2)-Xylene(3)-TMS (4) with UNIQUAC and UNIFAC predictions at 298.15 K.	47
<b>Table 5.12</b>	Comparison of experimental data for quinary system Hexane(1) - Octane(2)-Benzene(3)-Toluene(4)-TMS(5) with UNIQUAC and UNIFAC predictions.	48

<b>Table 5.13</b>	Simultaneous UNIQUAC parameters for Heptane – Toluene - TMS and Heptane-Xylene-TMS at 298.15K	48
<b>Table 5.14</b>	Comparison of Predictions using UNIFAC with experimental data for the systems Heptane-Toluene-TMS and Heptane-Xylene-TMS	49
<b>Table 5.15</b>	Simultaneous UNIQUAC parameters for Heptane-Toluene-TMS and Heptane-Xylene-TMS at 323.15K	49
<b>Table 5.16</b>	UNIQUAC binary interaction parameters for Heptane-Toluene-TMS	51
<b>Table 5.17</b>	UNIQUAC binary interaction parameters for Hexane-Benzene-TMS	52
<b>Table 5.18</b>	UNIQUAC parameters for Cyclohexane-Benzene-TMS	53
<b>Table 5.19</b>	Simultaneous UNIQUAC parameters for Heptane-Toluene-PC and Heptane-Xylene-PC at 298.15K	54
<b>Table 5.20</b>	UNIFAC group interaction parameters for PC with other main groups	54
<b>Table 5.21</b>	Comparison of experimental LLE data with predicted for five component system Hexane (1)–Heptane (2)–Toluene (3)–Xylene (4)–PC (5)	56
<b>Table 5.22</b>	UNIFAC group interaction parameters for NFM with other main groups	57
<b>Table 5.23</b>	Simultaneous UNIQUAC parameters for Heptane-Benzene-NFM, Heptane-Toluene-NFM and Heptane-Xylene-NFM at 311.5	58
<b>Table 5.24</b>	Estimated UNIQUAC interaction parameters for system Hexane–Benzene – DMSO	59
<b>Table 5.25</b>	Estimated UNIQUAC interaction parameters for Heptane–Toluene –DMSO at 298.15 K.	60
<b>Table 5.26</b>	Simultaneous UNIFAC group interaction parameters for Hexane-Benzene-DMSO and Heptane-Toluene-DMSO at 298.15K	60
<b>Table 5.27</b>	Estimated UNIQUAC interaction parameters for system Hexane – Benzene – TREG	62
<b>Table 5.28</b>	UNIQUAC binary interaction parameters for the system Heptane – Toluene – NMP at 298.15 K	63

<b>Table 5.29</b>	UNIQUAC binary interaction parameters for the system Cyclohexane – Benzene – DMF at 298.15 K	63
<b>Table 5.30</b>	UNIFAC group binary interaction parameters for NMP	63
<b>Table 5.31</b>	UNIQUAC binary interaction parameters for the system Heptane – Toluene – DEG at 298.15 K	64
<b>Table 6.1</b>	Interchange Energies of Solvents with CH <sub>2</sub> and ACH groups	70
<b>Table 6.2</b>	Performance of Solvents for Single Stage Extraction	71

# NOMENCLATURE

$a$	activity
$a$	binary interaction parameter
$c$	total number of components
$e$	difference between measured and true value
$\mathbf{e}$	vector of errors
$\mathbf{f}$	vector of functions
$K$	distribution coefficient
$L$	likelihood function
$m$	number of experimental data or tie-lines
$n$	number of measured variables
$p$	probability density
$R$	gas constant
$S$	selectivity
$v$	variance
$u$	interaction energy
$V$	variance-covariance matrix
$W$	weights
$x$	mole fraction
$\hat{x}$	estimated mole fraction
$\mathbf{z}$	vector of variable
$z$	mole fraction at the mid-point of a tie-line

## subscript and superscript

$c$	number of components
$I \text{ or } II$	phase $I$ or phase $II$
$i$	component $i$
$j$	phase $j$
$ij$	$ij$ pair of components or groups
$k$	experimental data or tie-line $k$
$\infty$	at infinite dilution

## Greek Symbols

$\gamma$	activity coefficient
$\theta$	vector of parameter
$\zeta$	vector of unknown true value
$\psi$	statistical parameter
$\varepsilon$	residual or error

## Other Symbols

PI	performance index
IE	interchange energy
<i>rmsd</i>	root mean squared deviation

## Chapter 1

# Introduction

Individual aromatic hydrocarbons such as benzene, toluene and xylenes find wide use and are considered essential in the modern organochemical industry. Aromatic hydrocarbons are key petrochemical raw materials and their importance and versatility seem to increase with time. From the light aromatics which are mainly benzene, toluene, xylene and generally termed as BTX, benzene is one relatively bright spot in the prevailing gloom of petrochemical industry. Since 1960 styrene, phenol and cyclohexane have clearly dominated the markets for benzene. Anthraquinone, DDT, detergent alkylate, solvent, maleic anhydride and aniline have vied for a position in this market. The other important uses of benzene today are nylon, Benzene-hexachloride, 2,4-D, bisphenol, dichlorobenzenes, pentachlorophenol and aspirin production. World benzene demand is around 31.7 MT and increasing at the rate of 3.6% per annum. In India, total supply is about 0.31 MT while its demand is about 0.85 MT.

Other aromatic compound toluene, once thought of largely as the basis for TNT, is now finding expanding use as a solvent and as a chemical intermediate in the production of diisocyanates, benzyl chloride, methyl styrene, saccharin and terephthalic acid etc. Toluene is also used as a blending stock for gasoline. The third aromatic compound xylenes also have many uses. Oxidation of various xylenes to phthalic, isophthalic and terephthalic acids is typical of new and growing uses of aromatics. The other uses of aromatics are dehydrogenation of ethylbenzene to produce styrene monomer.

The major sources for these aromatics from petroleum include straight –run or hydrogenated pyrolysis gasoline and catalytic reformats. These sources, apart from aromatics, contain large amount of other components also. The compound covers wide range of molecular weights and families (Paraffins, Isoparaffins, Olefins, Naphthenes, aromatics). Recovery and purification of these aromatic hydrocarbons is therefore an important commercial process. It is impossible to obtain a high purity of aromatics by distillation, which is the most widely used separation process in petroleum industry, due to overlapping boiling ranges of feed components. Many homogeneous binary azeotropes exist between aliphatic and aromatic hydrocarbons (Yorulmaz and Karpuzcu, 1985). Therefore liquid-liquid extraction will be a better choice

provided that components of the mixture show a suitable absolute solubility and sufficient difference in solubility in a solvent. And indeed the need to separate mixtures of aliphatic and aromatic hydrocarbons provided one of the first large-scale applications for solvent extraction. The original Eddeanu process used liquid sulfur dioxide for the removal of aromatics from lamp oil. The first major advance in aromatic separation occurred with the development of UDEX process, which used mixtures of polyethylene glycol and water as the solvent. Processes based on solvents Sulfolane, N-Methylpyrrolidone, dimethyl-sulfoxide and N-formylmorpholine followed this process.

The economics of solvent extraction process largely depends on the selection of solvent. The solvents in use now a days for aromatic extraction either have good selectivity for aromatics with simultaneously low solvent capacity or vice versa. Therefore it is customary to search for new solvents as well as to evaluate the performance of existing solvents. To evaluate the performance of solvents the important parameters are solvent selectivity, solvent capacity and solvent loss. Selectivity signifies the relative separation of two components, while the solvent capacity and solvent loss signifies the required flow rate of solvent and the required make up solvent respectively. By definition these parameters are calculated using the activity coefficients. The liquid phase activity coefficients are calculated using the thermodynamic model such as UNIQUAC, UNIFAC or NRTL that can give accurate determination of activity coefficients. These models require proper binary interaction parameters which can represent liquid – liquid equilibria for highly non – ideal liquid mixtures which are normally encountered in aromatic extraction.

Apart from evaluating the performance of solvents the methodologies known as molecular design of solvents, that are used for development of new solvents also require the accurate prediction of liquid – liquid equilibria. Therefore the availability of binary interaction parameters that can predict LLE accurately is of paramount importance for solvent selection. These parameters are yet not entirely available for systems encountered in aromatic extraction. For simulation and design of extractor also the availability of these parameters is a compulsion. Process simulators like ASPEN PLUS may produce drastic errors if used without accurately knowing these parameters.

These binary interaction parameters are generally estimated using experimental liquid – liquid equilibrium data. In case no experimental LLE data for systems of concern are available, the infinite dilution activity coefficients can be used for parameter estimation, although at the cost of accuracy. The methods used for parameter

estimation are **least square minimization** and **maximum likelihood approach**. In the former technique the weighted errors between experimental and predicted compositions is minimized while in the later approach a likelihood function is maximized. The drawbacks of least square minimization is that the proper weights are not known at the start of regression and improper selection of weights leads to unreliable parameters. The maximum likelihood approach, used nowadays, also has a serious drawback. In this approach the variances are fixed, generally on the basis of experimental precision. But the final values of variances after regression have been found to be inconsistent with fixed variances. Therefore this method may also lead to unreliable parameters.

It is possible to overcome this problem of maximum likelihood approach by recomputing the variance at each iteration of the optimization procedure. This recomputation of variance automatically weights the objective function thus promising most appropriate values of parameters are obtained.

It has been observed that the parameters obtained using different initial guess of parameter lead to different values (Vasquez and Whiting, 2000 [79] ). This is generally due to several local minima's in the objective function used for parameter estimation. Furthermore the binary parameters obtained for the same pair are found to be different for different ternary systems (Sorensen and Arlt, 1979 [72] ). For example the interaction parameters between pair Hexane – Benzene in system Hexane – benzene – TMS are different than in the system Hexane – Benzene – TREG as reported by (Sorensen and Arlt, 1979 [71] ). Therefore, these parameters are specific to the ternary system from which they have been estimated. And hence these parameters can not be used for other systems or for the multicomponent LLE prediction.

To avoid these problems, the parameter estimation approach is modified. Here the interaction parameters for different systems involving common pairs are estimated simultaneously. The objective function is modified to estimate the parameters simultaneously for different systems. In this way the problem of getting different sets of parameters for same pair has been eliminated. The regression approach is modified so that the parameters estimated from ternary LLE data are applicable for multicomponent prediction also.

### **Objectives of this Thesis**

1. To establish the methodology for UNIQUAC binary interaction parameter estimation from binary and ternary Liquid – Liquid Equilibrium data so that the parameters regressed should be applicable for multi-component LLE prediction (for aromatic extraction systems).
2. To establish the methodology for estimation of UNIFAC group interaction parameters from binary or ternary LLE data so that the parameters regressed can be used for multi-component prediction (for aromatic extraction systems).
3. To establish the effect of temperature on the UNIQUAC binary interaction parameters
4. To compare the performance of different solvents towards their extractability for aromatics by using estimated parameters for UNIQUAC.
5. To estimate the effects of aromatics content of feed, temperature, and solvent to feed ratio on selectivity and solvent power.
6. To categorize the different solvents according to there performance for aromatic extraction.

## Chapter 2

### LITERATURE REVIEW

#### 2.1: Solvent Selection Strategies

As compared to distillation, economics of liquid-liquid extraction is not well stabilized. The economical operation of liquid-liquid extraction largely depends on selection of solvent. A desirable solvent must have a high selectivity (relative separation between two components) for one hydrocarbon relative to the other. The selectivity of the solvent is determined by the activity coefficients of the hydrocarbons when dissolved in the solvent.

##### 2.1.1 Limiting activity coefficients

Infinite dilution activity coefficients play an important role in screening of potential solvents for liquid-liquid extraction. The solvents for aromatic recovery by either extractive distillation or extraction can be neatly rated in terms of the limiting activity coefficients for hexane and benzene as shown by ( Deal and Derr, 1964 [19] ). Limiting activity coefficients for hexane and benzene have been used by them to interrelate the capacity and selectivity for hydrocarbons for a broad series of solvents at 25 to 100 °C. Selectivity has been found to decrease with increasing temperature for almost all solvents. ( Deal and Derr, 1964 [19] ) have reported Sulfolane, Dimethyl-Sulfoxide and Dimethyl-Formamide as potential solvents for aromatic extraction.

A correlation for calculation of activity coefficients for different hydrocarbons when dissolved in excess of solvent has been given by ( Weimer and Prausnitz, 1965 [82] ). This correlation can be used for screening of the solvents when no experimental LLE data are available, as it requires only pure component properties. But this correlation has a limitation because of its dependency on regular solution theory. Because regular solution theory can not predict activity coefficients less than one, the use of this correlation is limited.

##### 2.1.2 Industrially used aromatic extraction processes

To compare the solvent performance for aromatic extraction, it will be beneficial to consider the existing aromatic extraction processes, apart from searching for new solvents. Extraction properties of Dimethyl-Sulfoxide (DMSO) as a solvent for

aromatic extraction have been discussed by Choffe et al., 1966. Extraction at ambient temperature using DMSO has been suggested operationally practical by them. This approach contrast against high temperature extraction processes (TETRA using Tetraethylene glycol, Udex using Diethyleneglycol water mixture etc.) used industrially (Hydrocarbon processing, 1970). Extraction properties of N-Formyl-Morpholine (NFM) used by FORMEX process has been discussed by Cinelli et al., 1972. Selectivity and capacity of NFM based on infinite dilution activity coefficients have been compared with that of NMP and Sulfolane. The selectivity of NFM have been reported better then that of NMP. Solvent capacity of NFM has been reported higher than that of Sulfolane, but the selectivity has been reported poorer than that of Sulfolane. Effect of water on solvent performance has also been discussed and it was found that presence of water increases selectivity, while it decreases the capacity. Extractability of Sulfolane and DMSO along with other sulfur group solvents (2-4-Dimethyl Sulfolane, Vinyl Sulfone, Tetramethylene Sulfoxide, Glycol Sulfite etc.) has been compared based on limiting activity coefficients by Rawat et al., 1976. Solvents having sulfone and sulfoxide groups were found to be better as compared to other sulfure group solvents. A comparison of existing aromatic extraction processes has been made (Bailes et al., 1976). Sulfolane has been found to posses largest selectivity value and NMP the largest capacity value. Extraction properties of Sulfolane used by Shell Process have been discussed in (Hydrocarbon Processing, 1982). Table 2.1 taken from Lo and Baird, 1980 gives an overview of existing aromatic extraction processes. This Table also gives operating conditions along with the solvents employed. Sulfolane used as a solvent by Shell process gives good selectivity and a favourable solvent capacity and thus leads to low solvent to feed ratio required. Initially the glycol used by Udex process was diethylene glycol with water, but later it was replaced by tetraethylene glycol and water mixture. Tetraethylene glycol and water mixtures are claimed to increase solvent capacity by a factor of 4 and also require no antifoaming agent. Tetraethylene glycol is also used in TETRA process of Union carbide, but without mixing with water. A two stage extraction process is used in the TETRA process. DMSO process of Institut Francais du Petrole (IFP) uses dimethyl-sulfoxide along with 2% water as solvent. High density and low freezing point of DMSO makes it economical to extract aromatics at ambient temperature. N-methyl-2-pyrrolidone of Arosolvan process is generally blended either with ethylene-glycol (40-50 wt %) or water (12-20 wt %) to increase the selectivity and to decrease the boiling point of the solvent. However addition of water

or ethylene- glycol slightly reduces the solvent capacity. The quantity of co-solvent required depends on the aromatics content of the feed.

Table 2.1. Processes used for extraction of aromatics

Process	Solvent	Operating conditions	Comments
Shell Process Universal Oil Products	Sulfolane	120 °C	High Selectivity and capacity of sulfolane leads to low solvent to feed ratio
Udex Process, Universal Oil Products	Diethylene-glycol/water mixture	150 °C	Tetraethylene glycol and water mixtures are claimed to increase capacity by a factor of 4. A two step distillation to recover BTX
Union Carbide Corporation	Tetraethylene-glycol (TETRA)	100 °C	The extract leaving the primary extractor is essentially free of feed aliphatic, and no further purification is necessary
Institut Francis du Petrole	Dimethyl-sulfoxide (DMSO)	Ambient	Solvent has low freezing point and is nontoxic and noncorrosive
Arosolvan Process, Lurgi	N-Methyl-2-Pyrrolidone (NMP)	NMP-ethylene – glycol (40-50 wt%), 60 °C	Either ethylene-glycol or water is used as cosolvent with NMP  The quantity of co-solvent required depends on the aromatics content of the feed.
		NMP-water water(12-20 wt%) 35 °C	
Formex Proess, SNAM Progetti [30]	N-Formyl-Morpholine (NFM)	40 °C	Low corrosion allows use of carbon steel equipment

### 2.1.3 Molecular Design of Solvents

On the basis of the UNIFAC group contribution, it was proposed to synthesize molecular structures with specific solvent properties for the separation of aromatic and paraffinic hydrocarbons by ( Gani and Brignole, 1983 [27] ). The method of molecular design of solvents has been well formulated in terms of **combination rules** and **target properties** ( Gani et. al., 1991 [26] ). It has been observed that large number of molecules can be generated by considering small number of **groups**. The size of combinatorial problem posed by the molecular synthesis procedure is reduced by **group selection** and by imposing **physical and molecular constraints** at different stages by ( Pretel et. al., 1994 [58] ). Limitations of UNIFAC arise due to non-availability of binary interaction parameters for groups. To circumvent this problem (Meniai and Newsham, 1995 [42]) has proposed method of calculating group binary interaction parameters, necessary for molecular design, using molecular graphics system.

### 2.2: Parameter Estimation

For evaluation of solvent performance for liquid-liquid extraction, the required parameters (selectivity, solvent power etc.) are calculated through prediction of liquid-liquid equilibria. For prediction a suitable thermodynamic model which can represent liquid-liquid equilibria should be used ( Bailes et. al., 1976 [7]). The excess free energy models such as NRTL the local composition model ( Renon & Prausnitz, 1968 [67] ) and the quasi chemical theory models UNIQUAC ( Abrams & Prausnitz, 1975 [1] ) and UNIFAC ( Fredenslund et al., 1975 [25] ) can represent liquid-liquid equilibria fairly well. These models require proper binary interaction parameters, which are generally obtained by regression of experimental data. Prediction of liquid-liquid equilibria is very much sensitive to the choice of parameters as compared to the vapour-liquid equilibria ( Abrams and Prausnitz, 1975 [1] ). For estimation of binary interaction parameters, binary LLE data for partially miscible systems and binary VLE data for completely miscible systems can be used. But for prediction of ternary liquid-liquid equilibria, which is normally used in liquid-liquid extraction calculations, the parameters obtained by using this approach have been found to be poor ( Varhegyi and Eon, 1977 [78]). This is mainly due to the fact that reduction of binary VLE data for

completely miscible systems cannot yield unique results unless the accuracy of the data is extremely high, much higher than usually encountered in typical experimental studies. Within the experimental error, many sets of binary parameters can equally well reproduce the binary VLE data (Abrams and Prausnitz, 1975). Furthermore if the binary interaction parameters thus obtained are used for multicomponent LLE prediction then the errors may be too large to justify (Anderson and Prausnitz, 1978). To avoid these discrepancies Varhegyi & Eon, 1977 have shown that ternary LLE data should be employed for regression of binary interaction parameters, in this way effect of VLE can be avoided. They have outlined the procedure to regress binary interaction parameters for NRTL model using ternary LLE data. Minimization of square of weighted errors between experimental and predicted compositions has been used to get the best fit. Varhegyi & Eon make no attempt to discern the physical meaning of the calculated parameters. The parameters have been treated only as correlation coefficients. To avoid the problem of getting different parameters for same pair, (Chen et al., 2000) have suggested to keep the parameters for a particular pair to be same for all systems.

A basic assumption of the least-square minimization is that the values of the independent variables are known without error. This assumption fails to account for the statistical properties of the independent variables, arbitrarily assigning them a zero standard deviation; therefore it does not utilize all available information in estimating the parameters. A more suitable method, which takes into account the errors in independent variables, will be the one based on maximum likelihood principle as suggested by Anderson et al., 1978. They have used maximum likelihood principle for the determination of model parameters from experimental data when all the measured variables are subject to error. Method has been applied for reduction of binary vapour-liquid equilibrium data. Sorensen and Arlt, 1979, have used maximum likelihood approach for regression of binary interaction parameters using ternary LLE data. Almost all of the maximum likelihood approaches currently used to regress the parameters of thermodynamic models fix the variances, converting the problem into a traditional weighted least square minimization. The variances are generally fixed on the basis of experimental error estimates (i.e. standard deviations). However such approaches lead to residual variances (between measured and calculated composition values) that are inconsistent with the fixed variances and thus, do not produce optimum parameters for prediction purposes. ( Vasquez & Whitting, 2000 )

have recently suggested a method, referred as IVEM (Inside Variance Estimation Method) which involves the re-computation of variance for each iteration of the optimization procedure, automatically re-weighting the objective function. This results in better parameter estimation and to a direct measure of uncertainty in the model prediction. In a later article (Vasquez & Whitting, 2000 [79] ) has shown the effect of regression approaches in the estimation of nonlinear model parameters on the predicted process performance.

## Chapter 3

### Solvent selection strategies

#### 3.1 Important characteristics of solvents for aromatic extraction

An efficient solvent for aromatic extraction should have sufficient solubility for aromatics, while very low solubility for non-aromatics. The solubility is mainly influenced by activity coefficients. Apart from solubility, the following properties of solvents, which can be characterized into primary and secondary properties, should be considered to evaluate the performance of solvents for extraction of aromatics.

##### Primary properties

- High Selectivity for aromatics
- High Capacity for aromatics
- Low Solvent Loss

##### Secondary properties

- High Density difference with Feed
- High Boiling Point
- Thermal Stability
- Sufficiently High Freezing Point
- Non Toxicity
- Environmentally acceptable
- Non Corrosiveness
- Low Price

Among these the first two, i.e. solvent selectivity and capacity are the two primary factors, which alter the efficiency of extraction process. For solvent selection these two parameters are considered primarily, with more importance given to selectivity. However, the best solvent is not necessarily that with highest selectivity value, since high selectivity often means low solvent capacity or solvent power for the extracted component. Solvent capacity has an even greater influence than selectivity on the selection of optimum extraction process because the capacity determines the flow rate of the circulating solvent and consequently the size of extractor. These two primary factors are defined as follows:

### 3.1.1 Solvent Selectivity

Selectivity is defined as the ratio of the distribution coefficients of the one aromatic component to that of one non-aromatic component in the system of solvent – aromatics – non-aromatics.

Hence,

$$\text{selectivity} = \frac{\text{Distribution coefficient for an eromatic}}{\text{Distribtution coefficient for a non-aromatic}}$$

or, in terms of notations (see nomenclature)

$$S_{ij} \equiv \frac{K_i}{K_j} = \frac{x_i^I x_j^{II}}{x_i^{II} x_j^I} \quad (3.1)$$

where subscripts ‘i’ and ‘j’ refer to the aromatic and non-aromatic components and superscripts I and II denote the extract and raffinate phases, respectively. Following the thermodynamic criteria for the phase equilibria, described later, it can be shown that (Mukhopadhyay, 1979 [46] ):

$$S_{ij} = \frac{\gamma_i^{II} \gamma_j^I}{\gamma_i^I \gamma_j^{II}} \quad (3.2)$$

### 3.1.2 Solvent Capacity

Solvent capacity or the solvent power is defined as the distribution coefficient of the solute (aromatics).

$$S_p \equiv K_i = \frac{x_i^I}{x_i^{II}} \quad (3.3)$$

following the thermodynamic criteria for phase equilibrium, it can be written as

$$S_p = \frac{\gamma_i^{II}}{\gamma_i^I} \quad (3.4)$$

It is usually observed that the solvents having high selectivity will have low solvent capacity and vice versa. Therefore a compromise between these two parameters

is necessary, for which a solvent selection criterion which will incorporate both these parameters is required. A simple criteria, the product of Selectivity and Solvent Capacity, called as performance index (PI) and defined as:

$$PI = S * S_p \quad (0.1)$$

was suggested by Brignole et al., 1986. However more terms such as Solvent Loss, Toxicity, etc. can be incorporated in the definition of PI depending on the particular needs.

## 3.2 Search for new solvents

Although most of the solvents commercially used possess good selectivity, their capacities are low. Therefore a high solvent flow rate is needed to achieve the desired recovery of aromatics. Because the extraction processes are found to be very expensive, it will be economical to search for new solvents, which can have favourable capacity apart from good selectivity. Good methodologies have been developed to search for new solvents for extraction as well as extractive distillation. The methodologies known as molecular design of solvents are widely used for development of solvents for separation processes.

### 3.2.1 Molecular Design of Solvents

Molecular design of solvents, originally developed to select entrainer for azeotropic distillation, has been extended for extraction solvent selection by Gani & Brignole, 1983. In this methodology the solvent molecules are designed from their constituent groups, so that the solvent will have the properties to achieve the desired separation. The solvent molecules are designed, keeping in view the desired properties such as selectivity, solvent power etc. These methodologies, primarily discussed by Gani & Brignole, 1983, Brignole et al. 1986, Gani et al, 1991, Pretel et al., 1994 and Constantinou et al, 1996 are based on the group contribution approach UNIFAC. In the UNIFAC method, the molecules are decomposed into groups and the properties of components are then calculated based on the group properties. A reverse technique is used for molecular design of solvents-here the molecules are generated with groups, which can have the desired properties. The overall procedure for molecular design of solvents can be broken into following steps:

#### (a) Classification of groups

The groups, which are to be considered for molecular design of solvent, are broadly categorized as terminal or intermediate groups ( Brignole et. al., 1986). Groups,

having single attachment for combination, are called terminal and having multiple attachment are called intermediate groups. These groups are further classified according to classes and categories ( Gani et. al., 1991 [28] ). The class of the group signifies the number of free attachments available to the group. The category of a class of groups signifies the degree of restrictions they have with respect to their linkage with other groups.

**(b) Selection of groups and target properties**

The target properties are selected according to the separation process for which, the solvent is to be designed. For extraction solvent design, the target properties may be, the selectivity, solvent power, solvent loss, or any combination of these. After selection of target properties, a sensitivity analysis of these properties with respect to all the groups is conducted, to pre-select not only a sub-set of groups but also, to pre-select certain type of compounds (aromatics, alcohols, ketones etc.). This analysis attempts to determine the most sensitive groups (called functional groups). The sensitivity analysis indicates the groups which are most likely (or least likely) to be present in the best molecular structures. The interchange energy, (IE), defined by Magnussen et al., 1981 [40] as an average of the binary interaction parameters, is used as a criteria for the selection of groups for a specific problem. A large positive value for the IE means solubility for the solute in the solvent. The interchange energy between groups  $i$  and  $j$  can be calculated from a summation of the group – interaction parameters  $a_{ij}$  and  $a_{ji}$  as given by Magnussen, 1981 [40]

$$a_{ij} = \frac{(u_{ij} - u_{jj})}{R}; \quad a_{ji} = \frac{(u_{ji} - u_{ii})}{R} \quad (3.6)$$

$$a_{ij} + a_{ji} = [u_{ij} - \frac{1}{2}(u_{ii} + u_{jj})] \frac{2}{R} = (IE) \cdot \frac{2}{R} \quad (3.7)$$

A small negative value of (IE) indicates good affinity between the solute group and the solvent. The difference in the values of IE for two groups in a solvent gives an indication of selectivity. If the differences are small and the values are negative, the ternary system will exhibit complete miscibility and separation with the solvent will be infeasible. The prediction of solvent properties requires the availability of UNIFAC binary interaction parameters. Therefore, the first criterion for the selection of groups is the availability of binary parameters for the synthesis groups with those of the feed mixture compounds.

On the basis of above the groups that should give good solvents for aromatic extraction have been identified. These groups are given in Table 3.1(a) along with references.

Table 3.1(a) Groups identified for aromatic extraction solvents

S. N.	Group	Reference
1	$CH_2O$ ,	Meniai & Newsham, 1999 [43]
2	$CH_3O$ ,	Gani & Brignole, 1983 [27]
3	$CH_2CN$	Brignole et. al., 1986 [9]
3	$CHNO_2$ ,	Gani & Brignole, 1983 [27] Brignole et. al., 1986 [9]
4	$CH_2NO_2$ ,	
5	$CH_3CO$	
6	$ACNH_2$ ,	Gani & Brignole, 1983 [27]
7	$CH_3COO$ ,	
8	$ACCH_2$	

#### (c) Formation of feasible chemical compounds (combination rules)

The generation of structures from the groups is subject to certain restrictions. These restrictions are imposed to prevent formation of unstable compounds or the appearance of new functional groups, like acetals, for which the prediction of the properties will be uncertain. The molecular structures to be formed must satisfy the primary condition that the final molecular structure cannot have any free attachments. Groups of certain categories have restrictions for their joining with other groups; these restrictions must be fulfilled. These restrictions, commonly referred to as combination rules, are well developed and tabulated.

#### (d) Evaluation of solvent properties and screening of compounds

The primary properties of a solvent for liquid-liquid extraction are selectivity and solvent capacity. The secondary properties are boiling point, density and viscosity etc. Once the chemically feasible molecular structures are formed, they can be tested for the constraints on the target properties. At this stage therefore the property prediction strategies are needed. The group contribution method UNIFAC is useful at this stage. However the binary interaction parameters for all the constituent groups of the generated solvents with the groups in feed should be available. Therefore the

availability of binary interaction parameters of all groups which are to be considered is of vital importance. But these parameters are still not available for large number of groups, which hinders the efficient use of molecular design of solvents.

A similar approach of molecular design of solvents developed initially by Meniai & Newsham 1992 [41], uses **molecular graphics system** for calculation of binary interaction energy for groups. A crude method of calculating binary interaction energy's, based on molecular graphics system coupled with Monte Carlo simulations has been proposed by Meniai & Newsham, 1995 [42]. The method has been tested for solvent selection for two industrial extraction processes Meniai & Newsham ,1999 [43]. Promising results have been obtained by this method.

### 3.3 Screening of Solvents based on Infinite Dilution Activity

#### Coefficients

The activity coefficient at infinite dilution (limiting activity coefficient) represents an important property, which is used in particular for the selection of selective solvents and for the reliable design of separation processes. The study of infinitely dilute solutions deserves considerable interest from both practical and theoretical point of view. In fact if we consider a mixture in which an important component is present at a very low concentration, the knowledge of the behavior of the dilute solution is essential for evaluating the recovery and separability of the components. The activity coefficient at infinite dilution characterizes the behavior of the solute molecule surrounded by the solvent: this indicates a maximum non-ideality whereas at finite concentrations the non-ideality is “diluted”, that is the activity coefficients assume values closer to unity. Therefore to be able to estimate the selectivity of a solvent, it is often sufficient to know the separation factor at infinite dilution. The activity coefficients at infinite dilution also provides a measure of separability of different solvents.

At infinite dilution, the parameters defined earlier for selection of solvents takes the form shown below.

#### 3.3.1: Selectivity at infinite dilution of solutes

$$S_{ij}^{\infty} = \left( \frac{\gamma_j^{\infty}}{\gamma_i^{\infty}} \right)^I \left( \frac{\gamma_i^{\infty}}{\gamma_j^{\infty}} \right)^{II} \quad (3.8)$$

At infinite dilution the ratio  $(\gamma_i^{\infty}/\gamma_j^{\infty})^{II}$ , i.e. in the nonpolar phase, becomes nearly equal to unity, as recommended by Deal & Derr, 1964 [19]. Therefore the selectivity at infinite dilution of solute approximately becomes

$$S_{ij}^{\infty} \cong \left( \frac{\gamma_j^{\infty}}{\gamma_i^{\infty}} \right)^I \quad (3.9)$$

### 3.3.2: Solvent capacity at infinite dilution of solute

The solvent capacity at infinite dilution of solute can be approximated by the relationship

$$S_p \cong \left( \frac{1}{\gamma_i^{\infty}} \right)^I \quad (3.10)$$

This approximate relation holds for almost all systems, involving aromatic and paraffin hydrocarbons, as proposed by Deal & Derr, 1964 [19].

### 3.3.3: Performance Index at infinite dilution of solute

On the basis of above definitions of solvent selectivity and capacity, the performance index defined in equation (3.5) for comparison of solvent performance can be approximated as follows.

$$PI^{\infty} = \left( \frac{\gamma_j^{\infty}}{(\gamma_i^{\infty})^2} \right)^I \quad (3.11)$$

These infinite dilution activity coefficients are generally obtained experimentally. The differential ebulliometry and gas liquid chromatography are the two most widely used techniques for experimental measurements of infinite dilution activity coefficients, with later gaining more importance now a days. If experimental value is not available for any promising solvent, it is possible to calculate these by pure component data only. The correlation's based on regular solution theory, such as one developed by Weimer & Prausnitz, 1965 [82], are useful for this purpose. The correlation developed by Weimer & Prausnitz, 1965 [82] is applicable for calculation of infinite dilution activity coefficients, for paraffin's, naphthenes and aromatic hydrocarbons in a large variety of polar solvents. Other generalized correlation's such as MOSCED (modified separation of cohesive energy density) gives good estimate of activity coefficient at infinite dilution ( Reid et. al.,1988 [66] ).

## 3.4: List of potential solvents and screening

Based on the above strategies and on the basis of industrially used solvents for aromatic extraction processes a list of potential solvents has been made. This list also

includes the solvents suggested by the method of molecular design of solvents reported by different authors.

These solvents have been screened based on their performance index at infinite dilution ( $PI^\infty$ ). For calculation of selectivity, solvent capacity and performance index calculation the experimental values of activity coefficients at infinite dilution ( $\gamma^\infty$ ) are used. The effect of temperature on selectivity and solvent capacity can also be looked at based on the variation of infinite dilution activity coefficients with temperature. The effect of temperature on selectivity, solvent capacity and performance index are given in Figure 3.1, Figure 3.2 and Figure 3.3 respectively. The references of the  $\gamma^\infty$  values used for calculation of selectivity and solvent capacity are reported in Table 3.1(b)

Table 3.1(b) Performance Index for Solvents along with References

S.N.	Solvent	$S^\infty$	$SP^\infty$	$(PI^\infty)$	Ref. for $\gamma^\infty$
1	N-Methyl-2Pyrrolidone (NMP)	12.59	0.96	12.11	[81] Weidlich, 1987
2	Sulfolane (TMS)	19.76	0.42	8.31	[44] Mollmann, 1997
3	N-Formyl-Morpholine (NFM)	16.01	0.45	7.80	[81] Weidlich, 1987
4	Dimethyl-Sulfoxide (DMSO)	20.36	0.30	6.17	[75] Tiegs, 1986
5	Dimthyl-Formamide (DMF)	12.12	0.44	5.30	[76] Tiegs, 1994
6	Tetraethylene-Glycol (TEG)	13.80	0.38	5.28	[75] Tiegs, 1986
7	Triethylene-Glycol (TREG)	17.50	0.22	3.95	[75] Tiegs, 1986
8	Propylene-Carbonate (PC)	12.19	0.30	3.66	[77] Tophoff, 1999
9	Diethylene-Glycol (DEG)	13.00	0.12	1.70	[28] Gmehling, 1986
10	N-Methyl-Formamide (NMF)	12.61	0.13	1.64	[30] Gmber, 1998

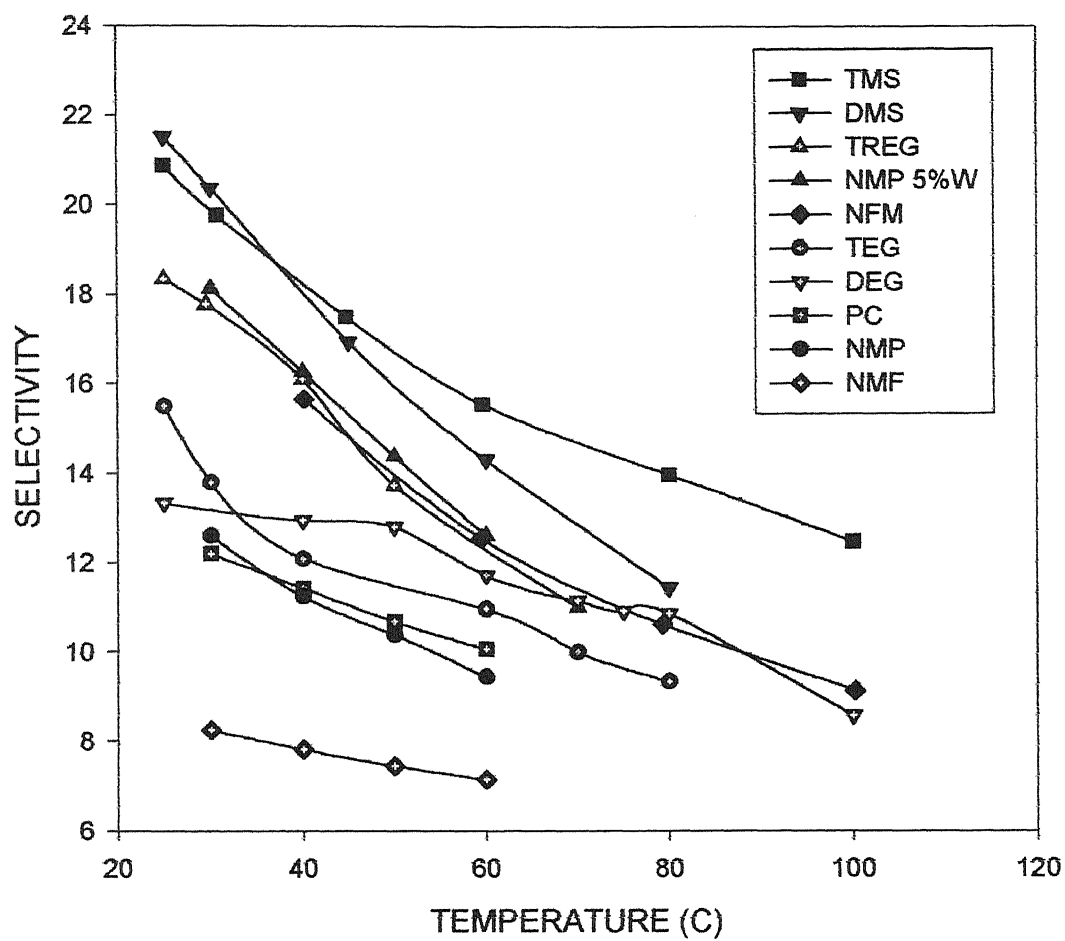


Fig.3.1: Variation of Selectivity in excess solvents with temperature

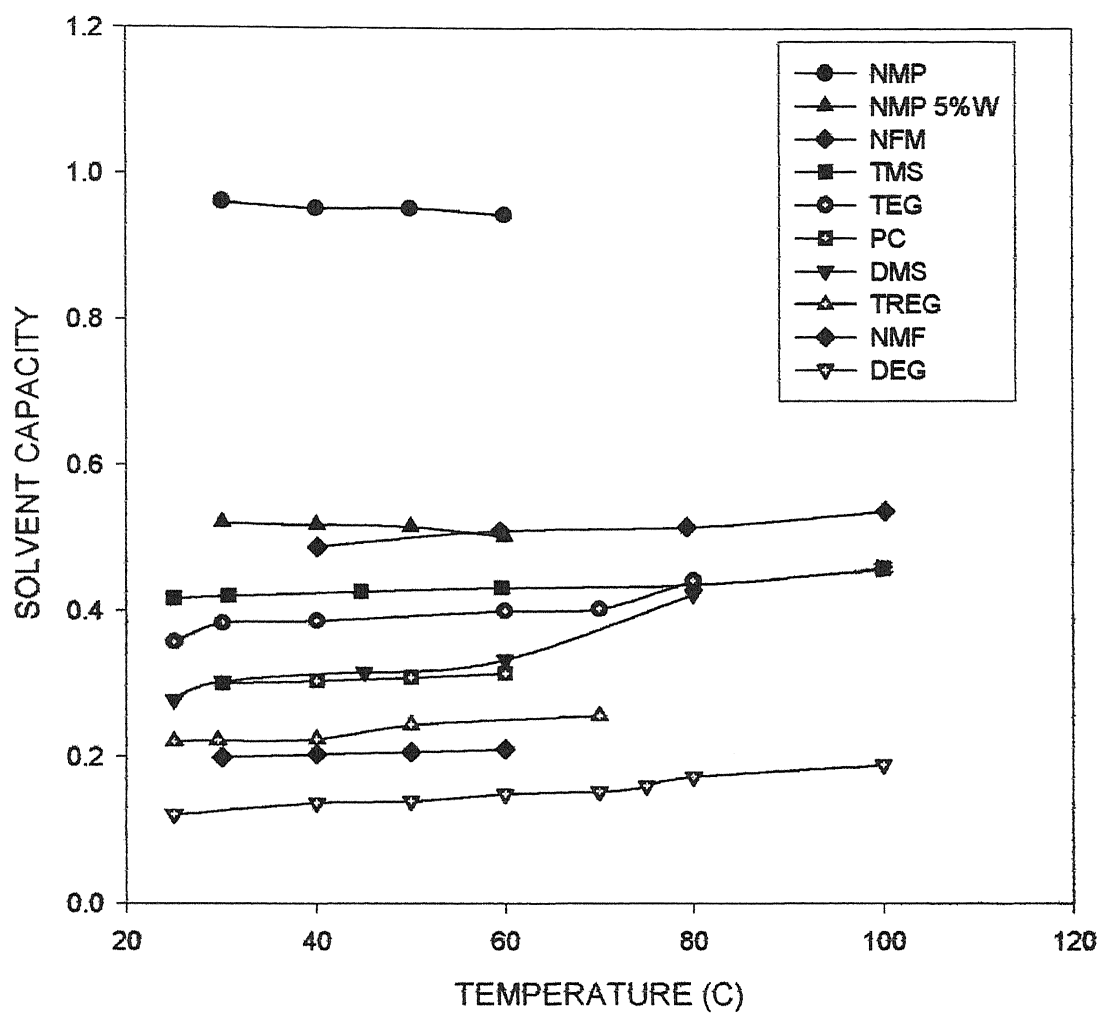


Fig.3.2: Variation of solvent capacity in the excess solvent with temperature

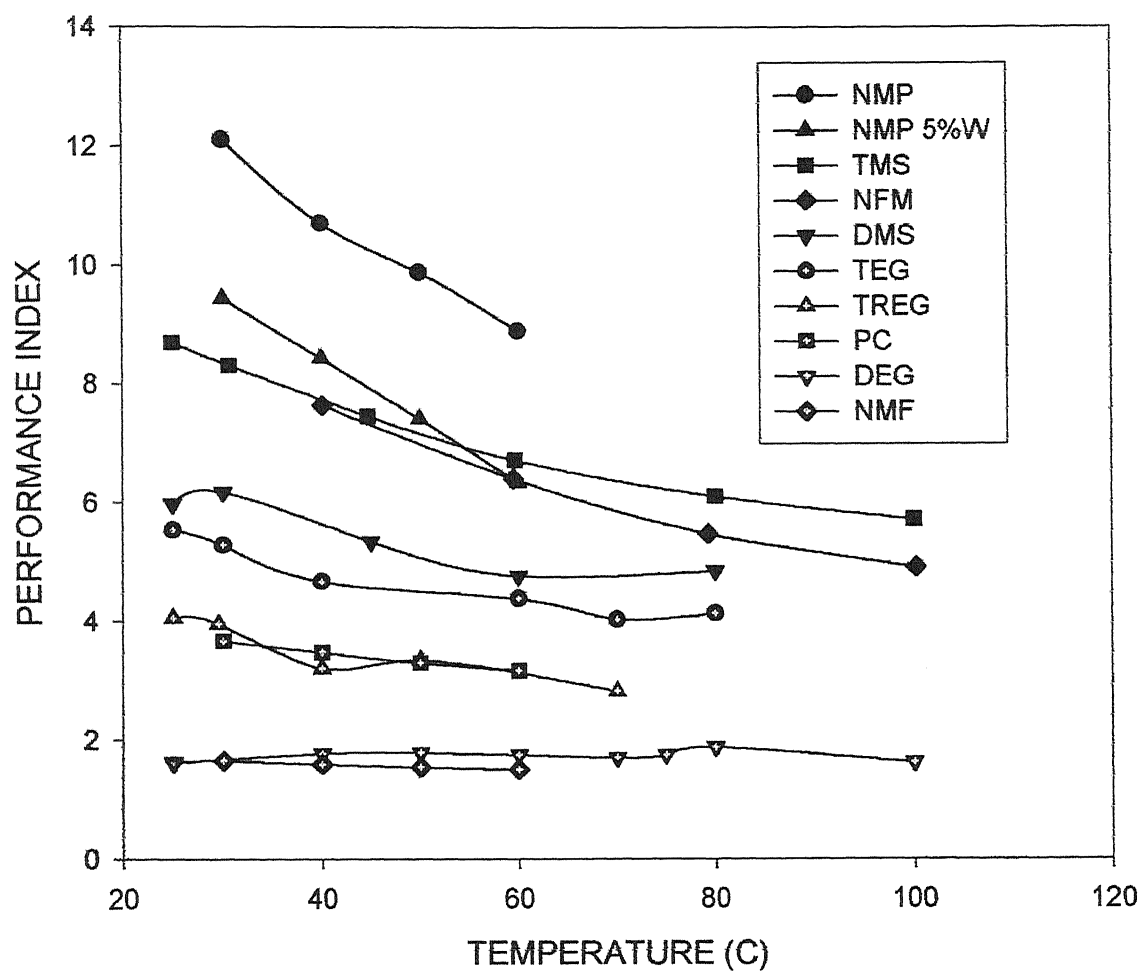


Fig.3.3: Variation of Performance Index in excess solvents with teperature

## Chapter 4

### PARAMETER ESTIMATION

The evaluation of solvent performance for analysis of aromatic extraction systems requires huge amount of experimental data. But experimental data on multi-component, (i.e. involving more than three components) liquid-liquid equilibria (LLE) of aromatic extraction systems are rather scarce. Therefore reliable prediction of multicomponent data from the knowledge of limited experimental data information is of vital importance to accurately evaluate the performance of solvents. Prediction of multi-component LLE and parameters for solvent performance evaluation requires the knowledge of activity coefficients in terms of compositions (Mukhopadhyay and Dongaonkar, 1983). Several models, such as UNIQUAC, UNIFAC, NRTL have been proposed to represent the composition dependence of the activity coefficients in mixtures (Walas, 1985). Among these three models the UNIQUAC model having two adjustable parameters gives almost similar predictions as compared to NRTL model having three adjustable parameters (Prausnitz et. al., 1980). All these models require binary interaction parameters. Liquid-liquid equilibria are found to be so sensitive to the value of these binary parameters that a small uncertainty in parameters can produce drastic errors in prediction of compositions (Gomis et. al., 1997). These model parameters are estimated by regression of experimental liquid-liquid equilibrium data. Small errors in experimental data can produce large uncertainty in regressed parameters, which in turn may lead to unreliable prediction (Vasquez & Whitting, 2000). Therefore the regression technique chosen should be capable of handling random errors in the experimental data. (Xin et al., 2000) has shown the effect of parameter regression approach on the prediction of liquid-liquid equilibria.

Our purpose here is to get thermodynamic model parameters, which can give accurate prediction of activity coefficients and compositions in nonideal liquid mixtures. Therefore for parameter estimation we should keep in view the minimization of errors between experimental and predicted compositions (or activities). Hence the regression of parameters is a minimization problem, from a mathematical point of view. The **two main approaches** to define objective function for minimization are **least square minimization** and **maximum likelihood principle**. Out of these two general

techniques, maximum likelihood approach takes into account the possible random errors in experiments (Prausnitz et. al., 1980 [56] ). However the least squares approach needs less computational effort.

Regression of binary interaction parameters needs predictions of composition variables for objective function calculation. Therefore the regression of liquid-liquid equilibria should start with solution of phase equilibria equations. The necessary condition for **phase equilibria**

$$\text{LLE:} \quad \gamma_i^I x_i^I = \gamma_i^{II} x_i^{II}, \quad i=1,2, \dots, c \quad (4.1)$$

along with **summation** equations,

$$\text{Summation:} \quad \sum_{i=1}^c x_i^I = 1 \quad \text{and} \quad \sum_{i=1}^c x_i^{II} = 1 \quad (4.2)$$

are solved at each iteration. The equation (4.1) is valid only when, same standard state fugacity is used in both the liquid phases. An acceptable assumption is that pressure, has no effect on the liquid-liquid equilibria, so the activity coefficients are functions only of temperature and compositions.

After prediction of phase equilibria using a suitable initial guess of parameters  $\theta$ , the objective function is calculated next.

#### 4.1 Least square minimization

Representing the parameters to be regressed by  $\theta$  vector, the most simple objective function using the least square technique, has the form

$$F_{11}(\theta) = \min_{\theta} \sum_{k=1}^m \sum_{i=1}^c \left[ x_{ik}^I \gamma_{ik}^I(x_{ik}^I, \theta) - x_{ik}^{II} \gamma_{ik}^{II}(x_{ik}^{II}, \theta) \right]^2 \quad (4.3)$$

In this objective function the summation of squared differences in activities of components in two phases is minimized. Many variations of the general objective function represented by equation (4.3) are possible, as given by ( Vasquez and Whiting, 2000 [79] ). Using the same approach, least square minimization of activity differences may take the form

$$F_{12}(\theta) = \min_{\theta} \sum_{k=1}^m \sum_{i=1}^c \left[ \ln a_{ik}^I(x_{ik}^I, \theta) - \ln a_{ik}^{II}(x_{ik}^{II}, \theta) \right]^2 \quad (4.4)$$

This objective function is a relative objective function, in which the ratio of activities is used. The objective function of equation (4.3) is an absolute objective function. These activity based objective functions have the common problem of not yielding good agreement with experimental results in general ( Anderson et. al., 1978 [2] ). However, they have very good convergence properties.

In the estimation of binary interaction parameters, our aim is to get the set of parameters for thermodynamic model, which can give good prediction of compositions of a multi-component mixture in both phases. Therefore more appropriate objective function should be the one which minimizes the errors between experimental and predicted compositions. The most general objective function of this type, with a least square minimization technique is

$$F_{13}(\theta) = \min_0 \sum_{k=1}^m \sum_{j=1}^2 \sum_{i=1}^n W_{ik}^j [x_{ik}^j - \hat{x}_{ik}^j]^2 \quad (4.5)$$

This type of objective function requires prediction of phase compositions, at each iteration of regression. For phase composition prediction and binodal curve prediction, the phase equilibria equations (4.1) along with summation equations (4.2) are solved simultaneously. And this prediction of phase equilibria is found to be computationally intensive and needs a qualified initial guess of parameters. Because of their good convergence, the activity based objective functions can be used at initial stage of regression procedure. The parameters obtained by minimization of objective functions  $F_{11}$  or  $F_{12}$  can be used as an initial guess for the objective function of equation  $F_{13}$ . Alternatively any other initial guess of parameters which can predict both phases can be used.

A basic assumption of least square method is that it discriminates between independent and dependent variables during regression. This method assumes that the independent variable (measured variable) is known without errors and only the dependent variables are susceptible to error. But this is not the case generally for the parameter estimation from liquid-liquid equilibrium data. Because the measured variables, i.e. the experimental compositions are always found to contain some errors (Prausnitz et. al., 1980 [57]), least square method cannot give the best estimate of parameters. This method does not account for statistical properties (standard deviations) of the independent variable. Since almost all models used for liquid-liquid equilibria are nonlinear in their adjustable parameters, the best estimates of these

parameters can be obtained from a formalized method, which properly treats the statistical behaviour of the errors associated with all experimental observations.

The methods based on maximum likelihood principle attempts properly to account for all measurement errors, as discussed by Anderson et al., 1978.

## **4.2 Maximum likelihood estimation**

It is usually assumed that there are two types of measurement errors: systematic and random. The formers are due to inherent bias in the measurement procedure resulting in a consistent deviation of the observable from its true value. Usually, an experimenter's skill and experience provide the only means of consistently detecting and avoiding the systematic errors. Random or statistical errors are assumed to be the result of a large number of small disturbances. Such errors have been found to be distributed according to simple laws that make it possible to treat them with statistical methods. A major consequence of these random errors is the corresponding presence of errors or uncertainties in the estimated parameters. Because of these errors in data, and also because of simplifications and assumptions in the model, it is not possible for a model to represent the experimental data exactly. However, a method of parameter estimation, which correctly utilizes all the pertinent information available will give a best fit of the model to the data and minimize the parameter uncertainty. The principle of maximum likelihood provides such estimation.

### **4.2.1 Maximum likelihood principle**

In the maximum-likelihood analysis, it is assumed that all measured data are subject to random errors. If the experiments were replicated, the average value for each replicated experimental point would approach some true value. Usually the distribution of a measured variable about its true value is approximated by the normal distribution, characterized by an associated variance. If there is any coupling between the measurement method, then there are also associated covariances between the measured variables. These variances and covariances must be known or estimated, although covariances are almost always assumed to be negligible (Anderson et al., 1978). It is customary to assume that the random errors in the different experiments are uncorrelated.

For each experiment, the true values of the measured variables are related by one or more constraints, those that account for material balance and phase equilibria. Because the number of data points exceeds the number of parameters to be estimated,

all constraints are not exactly satisfied for all experimental measurements. Optimum parameters and the true values corresponding to the experimental measurements must be found by satisfaction of an appropriate statistical criterion.

If this criterion is based on the maximum-likelihood principle, it leads to those parameter values that make the experimental observations appear most likely when taken as a whole. The likelihood function is defined as joint probability of the observed values of the variables, model parameters, and error variances. The best estimate of the model parameters and of the true values of the measured variables are those, that maximize this likelihood function with a normal distribution assumed for the experimental errors.

#### 4.2.2: Maximum likelihood estimation

The model for maximum likelihood parameter estimation takes the form of an implicit algebraic system of equations

$$\mathbf{f}(\boldsymbol{\theta}, \mathbf{z}) = \mathbf{0} \quad (4.6)$$

where  $\boldsymbol{\theta}$  is a vector of unknown parameters,  $\mathbf{z}$  is a vector of  $n$  experimentally measured variables, and  $\mathbf{f}$  represents the system of algebraic functions.

The measurements are related to the true values through

$$\mathbf{z}_k = \boldsymbol{\zeta}_k + \mathbf{e}_k \quad k = 1, \dots, m \quad (4.7)$$

where ‘ $m$ ’ is number of experimental data (tie lines), and  $\boldsymbol{\zeta}_k$  is vector of unknown true values of the experimentally measured variables,  $\mathbf{z}_k$ , at the  $k^{\text{th}}$  tie line, and  $\mathbf{e}_k$  is vector of errors.

The likelihood function ( $L$ ) is defined as the probability of the observed errors in all data points occurring given a set of statistical parameters ( $\psi$ ), i.e. the standard deviation for the distribution used to represent those errors. As it is generally assumed and is almost valid (Prausnitz et. al., 1980 [57]), the measurement errors from different data points are considered as uncorrelated or independent. Then, the joint probability density can be expressed as a product of the individual densities. Hence the likelihood function should be (Esposito & Floudas, 1998 [21])

$$L(\boldsymbol{\theta}, \psi) = \prod_{k=1}^m p(\mathbf{e}_k(\boldsymbol{\theta}) | \psi_k) \quad (4.8)$$

where  $p$  represents the probability density for the individual tie lines.

Further if we assume that the errors for  $n$  measured variables follow a normal distribution with zero mean and covariance matrix  $\mathbf{V}$ , we have

$$p(\mathbf{e}_k | \mathbf{V}_k) = \frac{(2\pi)^{-n/2}}{\sqrt{|\mathbf{V}_k|}} \exp\left[-\frac{1}{2} \mathbf{e}_k^T \mathbf{V}_k^{-1} \mathbf{e}_k\right] \quad (0.1)$$

Here  $n = 2$  for a binary system,  $n = 4$  for ternary system, and for a multi-component system  $n = 2*(c-1)$ , where  $c$  is the total number of components.

Hence, from equations (4.8) and (4.9) the logarithm of likelihood function  $L$  can be written as

$$\ln L(\theta, \psi) = -\frac{nm}{2} \ln 2\pi - \frac{1}{2} \sum_{k=1}^m \ln |\mathbf{V}_k| - \frac{1}{2} \sum_{k=1}^m \mathbf{e}_k^T \mathbf{V}_k^{-1} \mathbf{e}_k \quad (0.2)$$

The maximum likelihood estimator seeks to determine values for  $\theta$  and  $\psi$  which maximize  $L$ . In the estimation of binary interaction parameters for thermodynamic models it is always assumed that the errors in each experiment are known, equal, and independent, that is, the covariance matrix  $\mathbf{V}$ , is diagonal with elements  $v_{ii}$ , then the maximization of  $L$  from equation (0.2) is equivalent to

$$F_{21}(\theta, \psi) = \min \sum_{k=1}^m \sum_{i=1}^n e_{k,i}^2 v_{ii}^{-1} \quad (0.3)$$

where  $e_{k,i}$  is the  $i^{th}$  component of the vector  $\mathbf{e}_k$ , that is the error associated with the  $i^{th}$  variable in the  $k^{th}$  experiment.

This is the most widely used objective function for parameter estimation of nonlinear thermodynamic models by maximum likelihood function (Sorensen & Arlt, 1979). In this approach an priori estimate of variances are made based on experimental error, thus converting it to weighted least squares minimization. The variance-covariance matrix is fixed based on experimental precision. But as shown (Vasquez & Whiting, 2000), this method of using an priori estimate of variances is internally inconsistent because this estimate is not (in general) equal to the final values obtained from the residuals at the conclusion of the regression procedure. To avoid this inconsistency Vasquez and Whiting, 2000, suggested a method known as Inside Variance Estimation Method (IVEM). Although this method uses the objective function given by equation (4.10),  $\mathbf{V}_k$  is estimated from each iteration in the regression procedure. Thus, at the end of the optimization process, the statistical properties will be consistent with  $\mathbf{V}_k$ , guaranteeing that the most likely values of the  $\theta$  are found. In this method also it is assumed that errors are independent with each other,

so that the variance-covariance matrix is diagonal, with zero covariance terms. Therefore the maximization of  $L$  of equation (4.10) can be written as minimization of

$$F_{22}(\boldsymbol{\theta}, \psi) = \min(-\ln L) \equiv \min \left\{ \frac{mn}{2} \ln 2\pi + \frac{m}{2} \ln \left( \prod_{i=1}^n v_{ii} \right) + \frac{1}{2} \sum_{k=1}^m \mathbf{e}_k^T \mathbf{V}_k^{-1} \mathbf{e}_k \right\} \quad (4.12)$$

The regression process starts with a initial guess of parameters, which is used for phase envelope generation, and the objective function of equation (4.12) is minimized with any appropriate optimization technique. The predicted compositions are then compared with experimental ones either by objective function value or using root mean squared deviation (*rmsd*) defined as, for a ternary system

$$\text{rmsd} = 100 \left[ \sum_{k=1}^m \sum_{i=1}^n \sum_{j=1}^2 \frac{(x_{ik}^j - \hat{x}_{ik}^j)^2}{6m} \right]^{1/2} \quad (4.13)$$

here 6 in the denominator indicates the number of composition variables, 3 in each of the two phases. For a binary system it will be 4.

The algorithm for estimation of binary interaction parameters for thermodynamic models using liquid-liquid equilibria can be written as follows.

### 4.3: Algorithm for parameter estimation using LLE data

The main algorithm can be divided into following steps:

#### Step 1: Initial guess of parameters

A qualified initial guess of parameters, which is crucial for regression of LLE, can be obtained from different sources such as

- Aspen plus process simulator: Use parameter estimation run of Aspen plus to get UNIQUAC model parameters, using predictive UNIFAC for LLE
- Activity difference approach: Minimize objective function of either equation (4.3) or (4.4), with any initial guess.
- DECHEMA data bank: Interaction parameters for large number of systems have been reported in DECHEMA data bank (Sorensen & Arlt, 1980). Use common parameters as initial guess.
- Reported LLE parameters: Use any reported values of parameters from any other source in the literature as initial guess.
- Binary VLE parameters: If no liquid-liquid parameters are available, use binary VLE parameters for miscible pairs and binary LLE parameters for partially miscible pairs, as initial guess.

**Step 2: Predict phase equilibrium compositions (tie-lines)**

Use the initial guess of parameters obtained in step 1 to estimate activity coefficients using the thermodynamic models of concern (UNIQUAC/UNIFAC). Activity coefficients as a function of binary interaction parameters, composition and temperature are given in Appendix-A for UNIQUAC and UNIFAC models.

**Store** experimental tie lines into matrix **est\_tielines** (m, n)

**for all** experimental tie-lines **exp\_tielines** (m, n) **do**

**Compute** the estimated tie line corresponding to the experimental one.

**Estimate** the tie line, which passes through mid-point of experimental tie line. For this solve the simultaneous set of equations given below

For binary systems: **Solve**

$$\textbf{Phase equilibria:} \quad \hat{x}_i^I \gamma_i^I = \hat{x}_i^{II} \gamma_i^{II} \quad i = 1, 2 \quad (4.14)$$

along with

$$\textbf{Summation:} \quad \sum_{i=1}^2 \hat{x}_i^I = 1 \quad \text{and} \quad \sum_{i=1}^2 \hat{x}_i^{II} = 1 \quad (4.15)$$

for 4 composition variables, 2 in each of the two phases. For calculation of activity coefficients use the relations given in Appendix-A.

For ternary systems: **Solve**

$$\textbf{Phase equilibria:} \quad \hat{x}_i^I \gamma_i^I = \hat{x}_i^{II} \gamma_i^{II} \quad i = 1, 3 \quad (4.16)$$

along with

$$\textbf{Summation:} \quad \sum_{i=1}^3 \hat{x}_i^I = 1 \quad \text{and} \quad \sum_{i=1}^3 \hat{x}_i^{II} = 1 \quad (4.17)$$

and

$$\textbf{Predicted tie line:} \quad (z_2 - \hat{x}_2^I) = \frac{(\hat{x}_2^{II} - \hat{x}_2^I)}{(\hat{x}_1^{II} - \hat{x}_1^I)} (z_1 - \hat{x}_1^I) \quad (4.18)$$

for 6 composition variables, 3 in each of the two phases. Equation (4.18) is equation of tie line, which passes through the mid-point of the experimental tie line as shown in the figure. Where  $z_1$  and  $z_2$  are the compositions at the mid point of experimental tie lines as shown in Figure 4.1, and given by

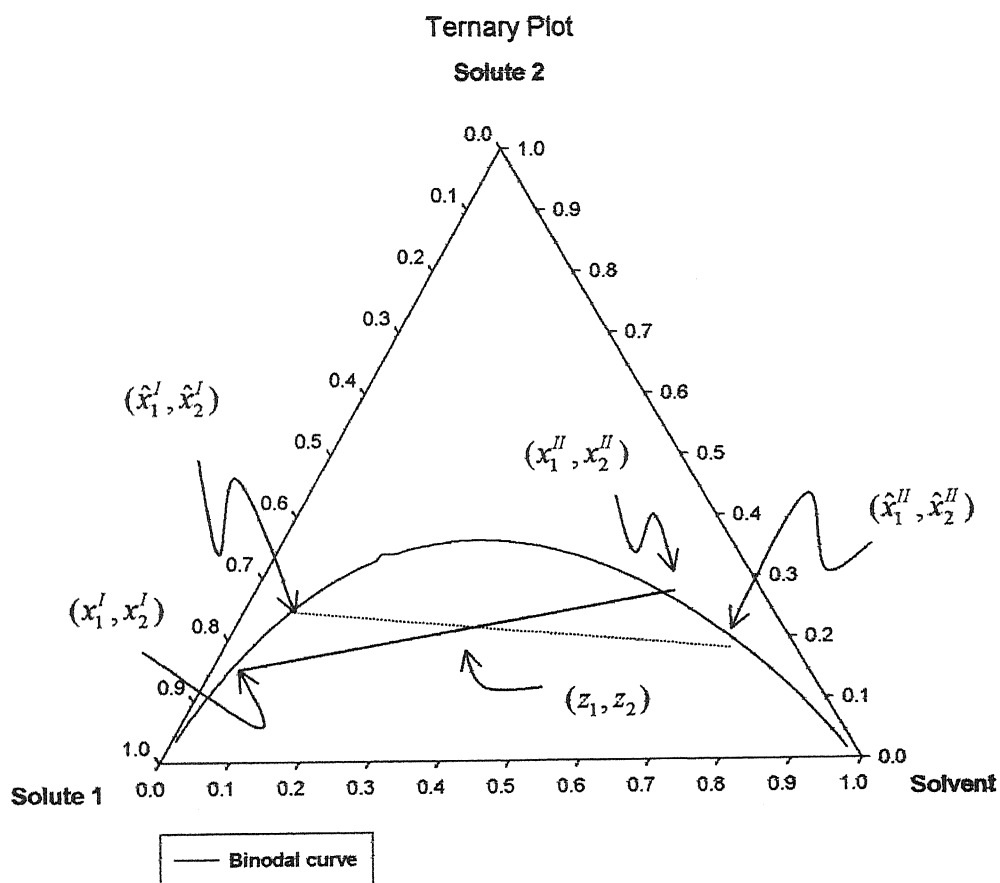


Figure 4.1 Ternary diagram with experimental and predicted tie line

$$z_1 = \frac{(x_1' + x_1'')}{2} \quad \text{and} \quad z_2 = \frac{(x_2' + x_2'')}{2}$$

**end**

**if**

above equations are solvable and give real solution of composition variables for all tie lines, then

**store** estimated tie lines in matrix **est\_tielines**(m, n), go to **step 3**

**else**

**change** the initial guess of parameters, go to **step 1**

**end**

### Step 3: Evaluate objective function

**Evaluate** the errors between **exp\_tielines** (m, n) and **est\_tielines** (m, n).

$$\varepsilon_{ki}(\theta) = \text{exp\_tielines}(k, i) - \text{est\_tielines}(k, i)$$

$$k = 1, \dots, m$$

$$i = 1, \dots, n$$

Take  $n = 2$  for binary systems and  $n = 4$  for ternary systems

**for all**  $i = 1, \dots, n$  **do**

**compute** the average error for the  $i^{th}$  component over all tie lines

$$\bar{\varepsilon}_i = \frac{\sum_{k=1}^m \varepsilon_{ki}}{m} \quad (4.19)$$

and the diagonal elements of variance in the matrix **V** given by

$$v_{ii} = \frac{\sum_{k=1}^m (\varepsilon_{ki} - \bar{\varepsilon}_i)^2}{(m-1)} \quad (4.20)$$

assign zero values to the off diagonal elements of **V**

**end**

**Evaluate** the objective function  $F_{22}$ , given by equation (4.12).

### Step 4: Minimize objective function

**Minimize** the objective function according to the optimization technique used.

**if**

objective function has reached a minimum then store parameters ( $\theta$ ) as the optimum parameters.

**else**

change  $\theta$  according to optimization procedure used, until minimum of objective function is reached.

**end**

**Calculate** the root mean squared deviation defined by equation (4.13)

Although the algorithm is written for inside variance estimation method (IVEM) based on maximum likelihood function, it can be used for least squares minimization technique also, with minor changes in step 3. For least squares technique the objective function is calculated directly after step 2 without calculating other statistical terms. The same algorithm can be used for parameter estimation of UNIQUAC as well as UNIFAC.

For minimization any suitable optimization technique can be used. The technique, used here is the simplex method, suggested by Nelder and Mead, 1964 [54]. Because this method does not require function derivative calculations, the round off errors will be low for this method (Anderson et. al., 1978 [2]).

## Chapter 5

### Parameter Estimation Results

The solvent performance for different solvents is evaluated on the basis of parameters such as selectivity, solvent capacity, solvent loss etc. as described in previous chapters. These parameters are defined in terms of activity coefficients, which in turn are calculated through thermodynamic models. The activity coefficient models, UNIQUAC and UNIFAC are widely accepted for activity coefficient prediction. These models are valuable only if the proper binary interaction parameters are available.

The feed, from which the aromatics are extracted, contains large number of compounds and several families (Paraffin, Isoparaffin, Olefin, Naphthene, Aromatic). The components present in the feed covers a large range of molecular weights. Therefore it is impossible to model exactly the aromatic extraction system. Furthermore the quantity of total aromatic and non-aromatic compounds present in the feed is also found to be different for different sources of naphtha. For evaluation of performance of solvents, the feed is generally assumed to be composed of key components. The number of key components used is also tentative and depends largely on the availability of experimental data. For the comparison of extractability of solvents, the feed is modeled as having one key aromatic component and one non-aromatic key component. More components can be added, based on the availability of experimental LLE data. The binary interaction parameters for the feed and solvent systems are then estimated. The systems used for parameter estimation here are given in Table 5.1(a). The multicomponent systems used for comparison of predictions using estimated parameters are listed in Table 5.1(b).

#### 5.1. Separate Estimation of parameters

For the estimation of binary interaction parameters the ternary data alone can be used as suggested by (Verhegyi and Eon, 1977 [78]) and implemented in DECHEMA data book (Sorensen and Arlt, 1979 [71]). However, the parameters obtained by this technique are found to be specific to that particular ternary system from which they were regressed. For example at the same temperature the interaction parameters for Hexane-Benzene pair have been found to be different in the system Hexane-Benzene-Sulfolane and Hexane-Benzene-Dimethylsulfoxide, as reported in DEHCMA. Similar behavior has been observed for all other systems also.

Table 5.1(a) Ternary Systems used for parameter estimation.

System Number	Ternary system	Temperature (K)
1	Hexane – Benzene- TMS	298.15, 323.15, 348.15, 373.15
2	Hexane – Toluene – TMS	298.15
3	Hexane – Xylene –TMS	298.15
4	Octane – Banzene – TMS	298.15
5	Octane – Toluene – TMS	298.15
6	Octane – Xylene – TMS	298.15
7	Heptane – Toluene – TMS	298.15, 323.15, 348.15, 373.15
8	Heptane – Xylene – TMS	298.15, 323.15
9	Cyclohexane – Benzene – TMS	298.15, 323.15, 348.15, 373.15
10	Heptane – Toleune – PC	298.15
11	Heptane – Xylene – PC	298.15
12	Heptane – Benzene – NFM	311.15
13	Heptane – Toluene – NFM	311.15
14	Heptane – Xylene – NFM	311.15
15	Hexane – Benzene – DMSO	298.15, 323.15
16	Heptane – Toluene – DMSO	298.15
17	Hexane – Benzene – TREG	293.15, 313.15, 333.15
18	Heptane – Toluene – NMP	298.15
19	Cyclohexane – Benzene – DMF	298.15
20	Heptane – Toluene – DEG	298.15

Table 5.1(b) Multicomponent systems used for comparison

System Number	Multicomponent systems	Temperature (K)
21	Hexane – Benzene – Xylene - TMS	298.15
22	Hexane – Octane – Benzene – TMS	298.15
23	Octane – Toluene – Xylene – TMS	298.15
24	Hexane – Octane – Benzene – Toluene – TMS	298.15
25	Hexane – Heptane – Toluene – Xylene - PC	298.15

Therefore the parameters obtained by this method can not be used for systems other than the one from which the parameters were regressed. Another problem with this method is that of initial guess. Because the parameter estimation is a minimization problem with several local minima's, different initial guesses lead to the different set of parameters (Prausnitz et. al., 1980 [57]). The above two problems are very common in parameter estimation, as it can be observed from the results obtained for the systems **Hexane-Benzene-Sulfolane** and **Hexane-Benzene-Dimethylsulfoxide**.

#### **5.1.1 Hexane-Benzene-TMS**

The UNIQUAC binary interaction parameters at 298.15 K for the Hexane-Benzene-TMS have been regressed using the ternary LLE data reported by (Chen et. al., 2000 [13]). Many different initial guesses of parameters have been tried. Parameters obtained for two different initial guesses are reported in Table 5.2. This Table also shows the objective function values and *rmsd* values. The initial guesses of parameters used for the regression have also been reported in Table 5.2. The first initial guess has been obtained from Aspen Plus Simulator, while the second from the minimization of activity difference objective function of equation (4.3). It can be observed from Table 5.2 that although two different initial guesses lead to two different sets of parameters, both sets represent the LLE data fairly well. The *rmsd* values and objective function values are also more or less same for the two initial guesses. Figure 5.1 and 5.2 compare the experimental and predicted compositions on ternary diagrams. It can be seen from these figures that the predicted tie line compare well with experimental tie lines for both the initial guesses.

#### **5.1.2 Hexane-Benzene-DMSO**

A similar behavior is observed for this system also. Table 5.3 gives the parameters regressed for this system, using two different initial guesses. The first initial guess is obtained through Aspen Plus, while the other is obtained using minimization of activity difference objective function of equation (4.3). The LLE data used for regression have been reported by ( Cassell et. al., 1989 [11] ) at a temperature of 298.15 K. For this system also the two different initial guesses of parameters lead to two different converged set of parameters. The *rmsd* values for both sets are comparable with each other, but the parameters obtained are quite different.

Hexane - Benzene - TMS at 298.15 K  
 Predicted using initial guess I (Table 5.2)

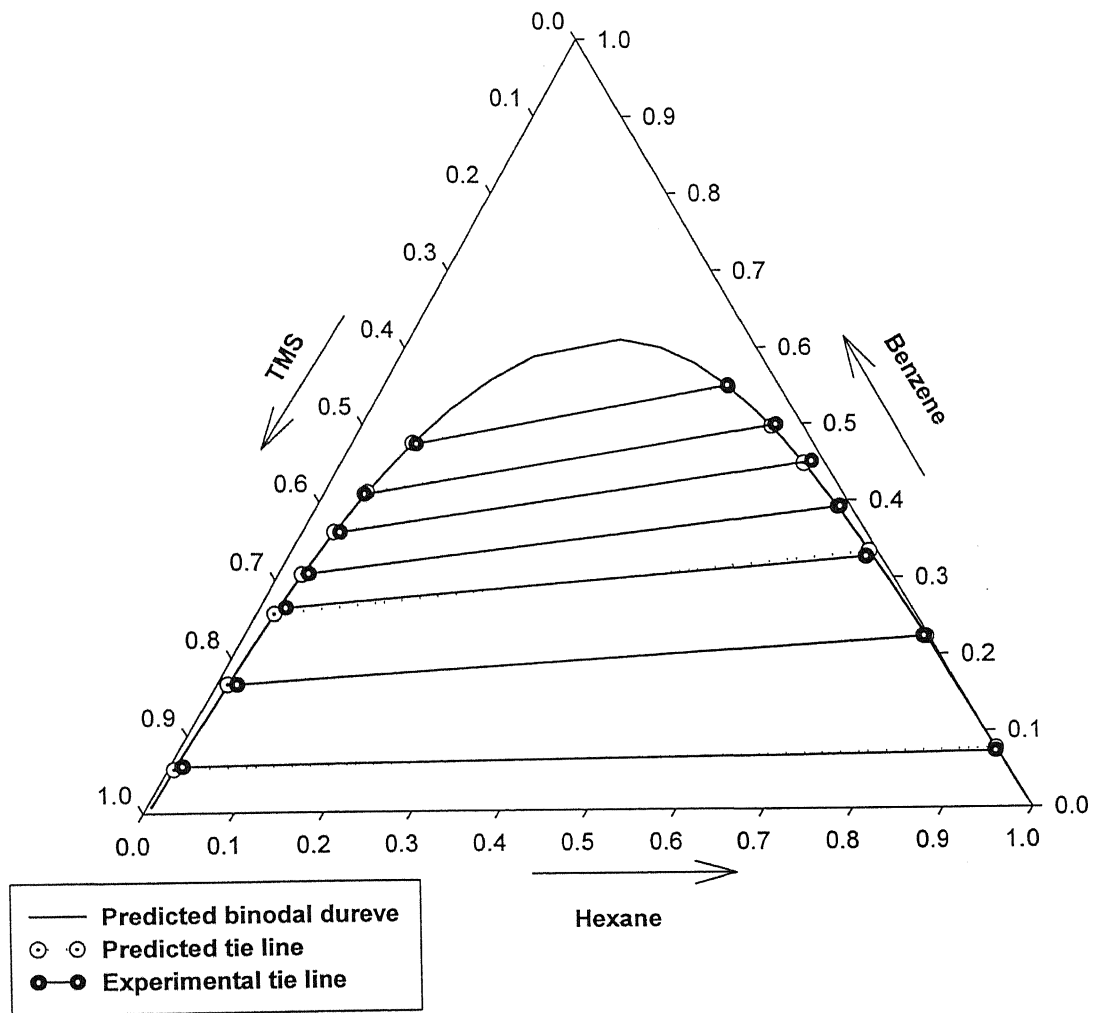


Fig: 5.1 Comparison of Predicted LLE with separate Estimation with initial guess I

Hexane - Benzene - TMS at 298.15 K  
 Predicted using initial guess II (Table 5.2)

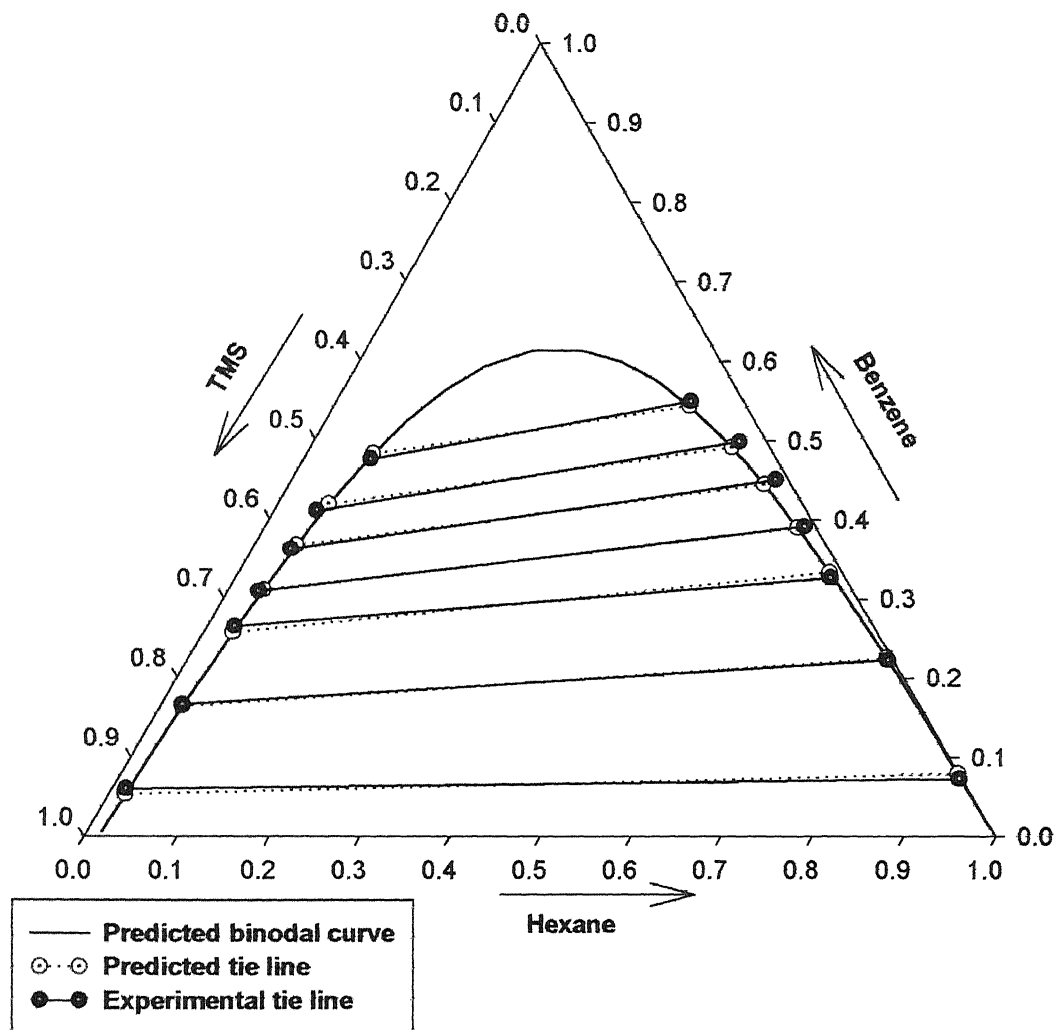


Fig: 5.2 Comparison of LLE predictions using separate estimation with initial guess II

Table 5.2 UNIQUAC parameters for Hexane-Benzene-TMS at 298.15 K

S.N.	Binary pair ij		Initial guess	Regressed parameters	Objective Function	No. of tie lines used	rmsd
	<i>i</i>	<i>j</i>	$a_{ij}$	$a_{ij}$	$-\ln L$	<i>m</i>	
1	Hexane	Benzene	-116.10	-369.0	-159.47	10	0.6016
	Hexane	TMS	561.40	708.46			
	Benzene	Hexane	157.95	529.90			
	Benzene	TMS	-21.90	-27.31			
	TMS	Hexane	67.84	133.40			
	TMS	Benzene	59.08	-41.20			
1	Hexane	Benzene	27.64	80.89	-143.87	10	0.8236
	Hexane	TMS	712.51	646.52			
	Benzene	Hexane	10.26	-32.41			
	Benzene	TMS	255.49	1.052			
	TMS	Hexane	87.52	64.44			
	TMS	Benzene	-64.86	113.45			

Table 5.3 UNIQUAC parameters for Hexane-Benzene-DMSO at 298.15 K

S.N.	Binary pair ij		Initial guess	Regressed parameters	Objective Function	No. of tie lines used	rmsd
	<i>i</i>	<i>j</i>	$a_{ij}$	$a_{ij}$	$-\ln L$		
15	Hexane	Benzene	-116.10	-116.11	-118.13	7	0.4954
	Hexane	DMSO	956.60	813.14			
	Benzene	Hexane	157.20	157.96			
	Benzene	DMSO	84.24	29.611			
	DMSO	Hexane	36.42	186.98			
	DMSO	Benzene	29.44	-81.47			
15	Hexane	Benzene	-155.46	-31.47	-104.48	7	0.3264
	Hexane	DMSO	799.49	4352.75			
	Benzene	Hexane	84.614	28.95			
	Benzene	DMSO	-7.313	88.46			
	DMSO	Hexane	55.456	22.32			
	DMSO	Benzene	-11.82	-21.97			

Furthermore, the parameters for common pair Hexane-Benzene between two systems are much different as summarized in Table 5.2 and 5.3. Therefore, parameters obtained using only one set of ternary data are found to be specific to that particular set of ternary system. Hence, these binary interaction parameters cannot be used directly to predict multi – component LLE of other systems involving these binaries. The parameters reported in DECHEMA (Sorensen and Arlt, 1979 [71]) also have the same problem.

To improve on above-mentioned problems, the parameter estimation procedure in this thesis has been modified so that the parameters between the common pairs in different systems should be same. The technique used here is that the parameters for the systems involving common pairs are regressed simultaneously, as discussed in next section.

## 5.2 Simultaneous Estimation of parameters involving common pairs

In the technique used in this thesis, the objective function of equation (4.12) is calculated for each ternary system, while keeping the parameters between common pairs same in all systems. The sum of the objective functions of all the systems is then minimized. For example the interaction parameters between the Hexane –TMS pair are kept same in all the systems involving this pair.

### 5.2.1 Systems with TMS

UNIQUAC parameters for **Hexane-Benzene-TMS(1)**, **Hexane-Toluene-TMS(2)** and **Hexane-Xylene-TMS(3)** systems have been estimated simultaneously. The ternary LLE data reported by (Chen et. al., 2000 [13]), at 298.15 K temperature have been used for regression. The objective function of the regression has been the sum of individual objective functions for three systems. To represent each ternary system, 6 binary interaction parameters are needed. Therefore for three ternary systems 18 binary parameters are required. But the Hexane-TMS binary pair is common to all three systems. Therefore for these three ternary systems only 14 parameters are required. In Table 5.4 the underlined components represent, the common binary pairs for which the interaction parameters were have to be same in all three systems. The initial guess of parameters have been obtained using UNIFAC-LL model of Aspen Plus. The regressed parameters along with the initial guesses are reported in Table 5.4. This Table also gives the objective function values after the regression. The predicted mole fractions are compared with experimental mole fraction, using the *rmsd* defined by equation (4.13) and shown in Figure 5.3. The predicted compositions, compares well with experimental compositions, as it can be observed from small *rmsd* values. Using the same approach UNIFAC group interaction parameters have also been obtained. The mutual interaction parameters for the groups CH<sub>2</sub>, ACH, and ACCH<sub>3</sub> are taken directly from the UNIFAC LLE group interaction parameters given by ( Magnussen et. al., 1981 [40] ) and are

Table 5.4 Simultaneous UNIQUAC parameters for Hexane – Benzene – TMS, Hexane – Toluene – TMS and Hexane – Xylene – TMS at 298.15 K

S.N.	Binary pair ij		Initial guess	Regressed parameters	Objective Function	No. of tie lines used	rmsd
	<i>i</i>	<i>j</i>	<i>a<sub>ij</sub></i>	<i>a<sub>ij</sub></i>	$-\ln L$	<i>m</i>	
1	Hexane	Benzene	-116.10	-155.47	-160.06	10	0.5698
	<u>Hexane</u>	<u>TMS</u>	<u>561.40</u>	<u>799.48</u>			
	Benzene	Hexane	157.95	84.61			
	Benzene	TMS	-21.90	-7.31			
	<u>TMS</u>	<u>Hexane</u>	<u>67.84</u>	<u>55.46</u>			
	TMS	Benzene	59.08	-11.82			
2	Hexane	Toluene	167.27	309.32	-183.23	10	0.3069
	<u>Hexane</u>	<u>TMS</u>	<u>561.40</u>	<u>799.48</u>			
	Toluene	Hexane	-137.20	-207.88			
	Toluene	TMS	47.06	136.04			
	<u>TMS</u>	<u>Hexane</u>	<u>67.84</u>	<u>55.46</u>			
	TMS	Toluene	79.69	-3.556			
3	Hexane	Xylene	272.432	303.15	-157.80	10	0.7353
	<u>Hexane</u>	<u>TMS</u>	<u>561.40</u>	<u>799.48</u>			
	Xylene	Hexane	-212.11	-196.06			
	Xylene	TMS	98.42	181.20			
	<u>TMS</u>	<u>Hexane</u>	<u>67.84</u>	<u>55.46</u>			
	TMS	Xylene	65.01	-5.14			
Total Objective function value $\equiv (-\ln L_1)+(-\ln L_2)+(-\ln L_3)=-502.1$							

kept fixed at the values shown in italic and interaction parameters of these groups with the TMS solvent have been estimated and given in Table 5.5. Breakdown of components of the three ternary systems, into UNIFAC groups is given in Table 5.6. The underlined values of the parameters have been directly taken from (Magnussen et. al., 1981 [40] ). The predictions using regressed UNIQUAC parameters are better than the UNIQUAC as can be observed from *rmsd* values.

The UNIFAC group parameters obtained using Hexane-Benzene-TMS, Hexane-Toluene-TMS and Hexane-Xylene-TMS can be used for the prediction of LLE for other systems also having paraffin, aromatic and TMS. The UNIFAC parameters obtained above has been directly used to predict the liquid-liquid equilibria for the systems Octane-Benzene-TMS, Octane-Toluene-TMS and Octane-Xylene-TMS systems. The predictions using these parameters is then compared with experimental data. Table 5.7 gives the comparison between experimental and predicted compositions

Hexane - Benzene TMS at 323.15 K  
 Predicted using simultaneously regressed parameters (Table 5.17)

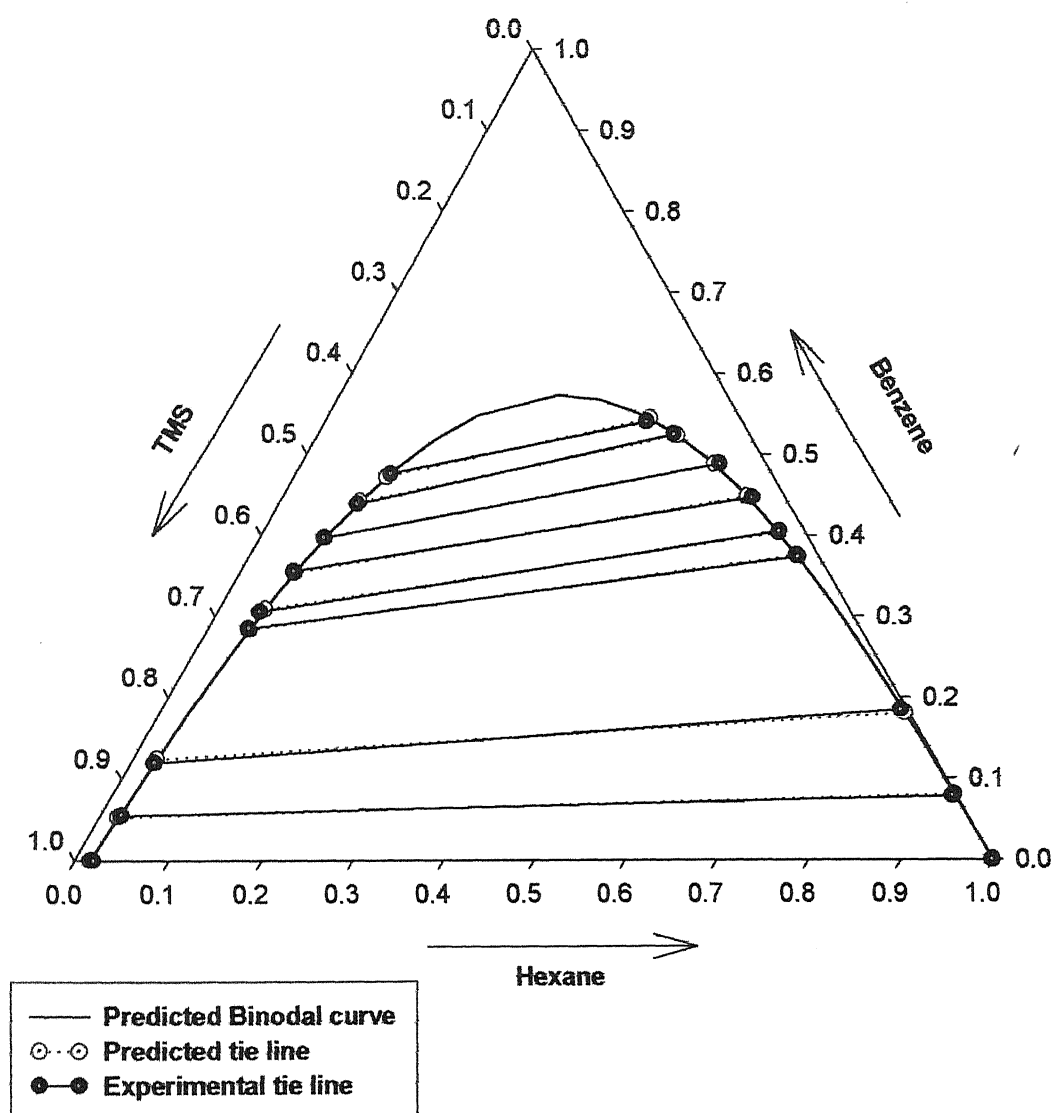


Fig. 5.3 Comparison of Predicted LLE using Simultaneous Estimation

in terms of *rmsd* values and objective function values. The predictions of LLE using these UNIFAC parameters compare well with experimental data. In the similar way the parameters for three ternary systems, **Octane-Benzene-TMS**, **Octane-Toluene-TMS** and **Octane-Xylene-TMS** have been regressed. The LLE data have been taken from ( Chen et. al., 2000 [13] ). Here also the parameters for the underlined binary pair (Octane-TMS and TMS-Octane) common for all three systems remain same during the regression procedure. Furthermore the parameters for the italicized pairs Benzene-TMS, Toluene-TMS and Xylene-TMS are kept fixed at their earlier regressed values as obtained in Tables 5.3. These parameters are not specific to the ternary system from

Table 5.5 UNIFAC group interaction parameters for TMS with other main groups

Binary Group Interaction Parameters $a_{ij}$					
$\begin{matrix} j \\ i \end{matrix}$	CH <sub>3</sub>	CH <sub>2</sub>	ACH	ACCH <sub>3</sub>	TMS
CH <sub>3</sub>	0	0	-114.80	-115.70	665.45
CH <sub>2</sub>	0	0	-114.80	-115.70	665.45
<u>ACH</u>	156.50	156.50	0	167.00	36.30
ACCH <sub>3</sub>	104.40	104.40	-146.80	0	236.58
<u>TMS</u>	52.39	52.39	54.33	9.93	0

Table 5.6 Comparison of Predictions using UNIFAC with experimental data for the systems Hexane-Benzene-TMS, Hexane-Toluene-TMS and Hexane-Xylene-TMS

S. N.	Ternary System	UNIFAC Group assignment	Objective Function	rmsd
1	Hexane Benzene TMS	2 CH <sub>3</sub> , 4 CH <sub>2</sub> 6 ACH 1 TMS	-134.33	0.9550
2	Hexane Toluene TMS	2 CH <sub>3</sub> , 4 CH <sub>2</sub> 5 ACH, 1 ACCH <sub>3</sub> 1 TMS	-161.18	0.6022
3	Hexane Xylene TMS	2 CH <sub>3</sub> , 4 CH <sub>2</sub> 4 ACH, 2 ACCH <sub>3</sub> 1 TMS	-146.74	0.9414

Table 5.7 Comparison of Predictions using UNIFAC with experimental data for the systems Octane-Benzene-TMS, Octane-Toluene-TMS and Octane-Xylene-TMS

S. N.	Ternary System	Group assignment	Objective Function	rmsd
1	Octane Benzene TMS	2 CH <sub>3</sub> , 6 CH <sub>2</sub> 6 ACH 1 TMS	-121.25	1.012
2	Octane Toluene TMS	2 CH <sub>3</sub> , 6 CH <sub>2</sub> 5 ACH, 1 ACCH <sub>3</sub> 1 TMS	-136.93	0.5208
3	Octane Xylene TMS	2 CH <sub>3</sub> , 6 CH <sub>2</sub> 4 ACH, 2 ACCH <sub>3</sub> 1 TMS	-126.69	0.7735

where they have been regressed. Table 5.8 shows the regressed parameters at 298.15 K along with the initial guesses. The parameters obtained for systems (1, 2 and 3 given in Table 5.4) having Hexane has been taken as initial guess. The predictions using regressed parameters compares well with experimental data as can be observed from reported *rmsd*.

The validity of parameters regressed can be checked by comparison of prediction of multi-component LLE using these parameters with experimental data. Multi-component data for the quaternary systems **Hexane-Benzene-Xylene-TMS** and **Hexane-Octane-Benzene-TMS** have been used, because these systems involve same binary pairs for which the interaction parameters have been obtained. Experimental LLE data for these two systems have been reported by (Chen et. al., 2000 [14]). Table 5.9 compares the experimental compositions with predicted compositions using the UNIFAC parameters reported in Table 5.4. No parameters other than the reported in Table 5.4, are required for this quaternary system. The interaction parameters between Benzene and Xylene are kept zero, because this pair represents a fairly ideal solution (Chen et. al., 2000 [14]). Table 5.9 also gives the prediction of compositions using the UNIFAC method with regressed parameters obtained in Table 5.4. The *rmsd* values have been estimated for quaternary predictions and are reported in Table 5.9. For a quaternary system

$$rmsd = 100 \left[ \sum_{k=1}^m \sum_{i=1}^4 \sum_{j=1}^2 \frac{(x_{ik}^j - \hat{x}_{ik}^j)^2}{8m} \right]^{1/2} \quad (5.1)$$

Predictions of quaternary LLE using the regressed parameters have also been compared with experimental data for the system **Hexane-Octane-Benzene-TMS**. Experimental data have been reported by (Chen et. al., 2000 [14]). For prediction UNIQUAC parameters from Table 5.4 and Table 5.8 have been used. The interaction parameters between pair Hexane-Octane have been kept zero, as suggested by (Salem et. al., 1994 [70]). The predicted as well as experimental mole fractions are given in Table 5.10. These parameters have also been used to predict LLE for system **Octane-Toluene-Xylene-TMS** at 298.15 K for which the experimental LLE data have been

Table 5.8 Simultaneous UNIQUAC parameters for Octane – Benzene – TMS, Octane – Toluene – TMS, and Octane – Xylene – TMS at 298.15 K

S.N.	Binary pair ij		Initial guess	Regressed parameters	Objective Function	No. of tie lines used	rmsd
	<i>i</i>	<i>j</i>	$a_{ij}$	$a_{ij}$	$-\ln L$	$m$	
1	Octane	Benzene	-155.47	-165.43	-164.33	10	0.6485
	<u>Octane</u>	<u>TMS</u>	799.48	859.29			
	Benzene	Octane	84.61	111.67			
	Benzene	TMS	-7.31	-7.31			
	<u>TMS</u>	<u>Octane</u>	55.46	34.23			
	TMS	Benzene	-11.82	-11.82			
2	Octane	Toluene	309.32	269.86	-158.95	9	0.3973
	<u>Octane</u>	<u>TMS</u>	799.48	859.29			
	Toluene	Octane	-207.88	-190.21			
	Toluene	TMS	136.04	136.04			
	<u>TMS</u>	<u>Octane</u>	55.46	34.23			
	TMS	Toluene	-3.56	-3.55624			
3	Octane	Xylene	303.15	320.43	-154.54	10	0.5172
	<u>Octane</u>	<u>TMS</u>	799.48	859.29			
	Xylene	Octane	-196.06	-204.48			
	Xylene	TMS	181.20	181.20			
	<u>TMS</u>	<u>Octane</u>	55.456	34.23			
	TMS	Xylene	-5.14	-5.14			
Total Objective function value $\equiv (-\ln L_1) + (-\ln L_2) + (-\ln L_3) = -477.82$							

reported (Chen et. al., 2000 [14]). The predicted mole fractions using the UNIQUAC and UNIFAC are given in Table 5.11 along with the experimental LLE data. The *rmsd* values are also given.

Table 5.9 Comparison of experimental data for quaternary system Hexane(1)-Benzene(2)-Xylene(3)-TMS(4) with UNIQUAC and UNIFAC predictions.

Tie line		Raffinate phase				Extract phase			
		$x_1^I$	$x_2^I$	$x_3^I$	$x_4^I$	$x_1^{II}$	$x_2^{II}$	$x_3^{II}$	$x_4^{II}$
1	Exptl.*	0.857	0.076	0.051	0.017	0.016	0.052	0.01	0.921
	UNIQUAC	0.874	0.077	0.047	0.001	0.017	0.051	0.015	0.917
	UNIFAC	0.869	0.079	0.049	0.002	0.020	0.049	0.012	0.919
2	Exptl.	0.709	0.135	0.143	0.013	0.021	0.094	0.043	0.841
	UNIQUAC	0.713	0.139	0.142	0.006	0.021	0.091	0.044	0.844
	UNIFAC	0.709	0.138	0.145	0.008	0.023	0.091	0.041	0.845
3	Exptl.	0.575	0.266	0.134	0.025	0.028	0.199	0.046	0.727
	UNIQUAC	0.576	0.270	0.135	0.019	0.029	0.195	0.045	0.730
	UNIFAC	0.577	0.271	0.133	0.019	0.031	0.195	0.047	0.726
4	Exptl.	0.450	0.156	0.356	0.038	0.026	0.107	0.135	0.732
	UNIQUAC	0.451	0.154	0.358	0.037	0.029	0.109	0.135	0.726
	UNIFAC	0.448	0.154	0.358	0.040	0.028	0.109	0.133	0.729
5	Exptl.	0.316	0.497	0.098	0.088	0.083	0.432	0.062	0.423
	UNIQUAC	0.310	0.493	0.102	0.095	0.074	0.432	0.055	0.439
	UNIFAC	0.322	0.495	0.098	0.085	0.077	0.434	0.062	0.427
$rmsd$ value using UNIQUAC = 0.588 $rmsd$ value using UNIFAC = 0.4156 $rmsd$ value reported for NRTL = 0.69 (*Chen et. al., 2000 [14] )									

Predictions using the regressed UNIQUAC and UNIFAC interaction parameters have been compared with experimental data for a five component system. LLE data for the quinary system Hexane-Octane-Toluene-Xylene-TMS have been reported by ( Chen et. al., 2000 [14] ). The predicted LLE data by UNIQUAC and UNIFAC are compared with experimental data in the Table 5.12. For prediction using UNIQUAC the parameters reported in Table 5.4 and Table 5.8 have been used. The interaction parameters between pair Hexane-Octane and between pair Benzene-Toluene have been kept zero, as earlier. For prediction using UNIFAC the group parameters reported in Table 5.5 have been used. The *rmsd* values are also given for

comparison with reported *rmsd* values using NRTL specific parameters. Predictions of both UNIFAC and UNIQUAC are in well agreement with experimental LLE data.

Using the similar approach the UNIQUAC parameters at 298.15 K for systems **Heptane-Toluene-TMS** and **Heptane-Xylene-TMS** have been estimated using the LLE data of Chen et al., 2000. The parameters for Toluene-TMS and Xylene-TMS pairs have been fixed at the values obtained earlier Table 5.3. Table 5.12 gives the regressed parameters along with initial guesses used. The *rmsd* values for the two systems are also reported in the Table 5.12. The parameters obtained for Hexane-Toluene-TMS and Hexane-Xylene-TMS have been used as initial guess.

Table 5.10 Comparison of experimental data for quaternary system Hexane(1)-Octane(2)-Benzene(3)-TMS(4) with UNIQUAC and UNIFAC predictions.

Tie line		Raffinate phase				Extract phase			
		$x_1^I$	$x_2^I$	$x_3^I$	$x_4^I$	$x_1^{II}$	$x_2^{II}$	$x_3^{II}$	$x_4^{II}$
1	Exptl.*	0.173	0.655	0.153	0.019	0.020	0.007	0.104	0.869
	UNIQUAC	0.189	0.656	0.153	0.001	0.004	0.007	0.104	0.885
	UNIFAC	0.186	0.648	0.162	0.002	0.004	0.006	0.094	0.895
2	Exptl.	0.552	0.187	0.240	0.021	0.017	0.003	0.181	0.799
	UNIQUAC	0.562	0.190	0.244	0.004	0.018	0.003	0.179	0.800
	UNIFAC	0.552	0.188	0.253	0.005	0.019	0.003	0.167	0.810
3	Exptl.	0.288	0.353	0.340	0.019	0.011	0.009	0.260	0.720
	UNIQUAC	0.289	0.357	0.344	0.009	0.013	0.009	0.257	0.720
	UNIFAC	0.283	0.351	0.355	0.010	0.014	0.008	0.244	0.734
4	Exptl.	0.282	0.171	0.524	0.023	0.031	0.012	0.426	0.531
	UNIQUAC	0.275	0.166	0.519	0.039	0.035	0.015	0.429	0.520
	UNIFAC	0.273	0.167	0.523	0.036	0.034	0.012	0.424	0.530
5	Exptl.	0.154	0.138	0.618	0.100	0.053	0.036	0.563	0.347
	UNIQUAC	0.149	0.130	0.618	0.102	0.053	0.039	0.559	0.349
	UNIFAC	0.158	0.141	0.622	0.079	0.046	0.030	0.558	0.366
$rmsd$ using UNIQUAC = 0.7621 $rmsd$ using UNIFAC = 1.05655 $rmsd$ reported using NRTL = 0.99 (*Chen et. al., 2000)									

The LLE for the systems Heptane-Toluene-TMS and Heptane-Xylene-TMS have been predicted using the estimated UNIFAC parameters. The predictions have been compared with experimental data in Table 5.14. The *rmsd* values are comparable

with the *rmsd* values obtained using the UNIQUAC parameters regressed from the same set of data. These and previous results show the wide range of applicability of the regressed UNIFAC parameters.

The same procedure is adopted for higher temperature data. The liquid-liquid equilibrium data given by Cassell et al., 1989 for **Heptane-Toluene-TMS** at 323.15 K and by Sorensen and Arlt, 1979 for **Heptane-Xylene-TMS** at 323.15 K have been used to estimate the UNIQUAC binary interaction parameters. The regressed parameters along with initial guesses are reported in Table 5.15. Parameters between underlined pairs are common to both the systems. Parameters at 298.15 K, reported in Table 5.13 have been used as initial guess. The *rmsd* values and the objective functions are also reported in Table 5.15.

Table 5.11 Comparison of experimental data for quaternary system Octane(1)-Toluene(2)-Xylene(3)-TMS (4) with UNIQUAC and UNIFAC predictions at 298.15 K.

Tie line		Raffinate phase				Extract phase			
		$x_1^I$	$x_2^I$	$x_3^I$	$x_4^I$	$x_1^{II}$	$x_2^{II}$	$x_3^{II}$	$x_4^{II}$
1	Exptl.*	0.649	0.154	0.184	0.013	0.007	0.058	0.041	0.894
	UNIQUAC	0.668	0.155	0.172	0.005	0.01	0.06	0.057	0.873
	UNIFAC	0.658	0.154	0.18	0.008	0.008	0.06	0.047	0.886
2	Exptl.	0.548	0.244	0.187	0.022	0.011	0.105	0.057	0.827
	UNIQUAC	0.559	0.247	0.183	0.011	0.011	0.105	0.064	0.82
	UNIFAC	0.552	0.244	0.189	0.016	0.009	0.105	0.056	0.83
3	Exptl.	0.517	0.182	0.274	0.027	0.01	0.075	0.088	0.827
	UNIQUAC	0.53	0.183	0.273	0.014	0.012	0.077	0.093	0.818
	UNIFAC	0.522	0.18	0.28	0.018	0.009	0.078	0.084	0.83
4	Exptl.	0.366	0.425	0.178	0.031	0.017	0.217	0.069	0.697
	UNIQUAC	0.365	0.422	0.173	0.039	0.017	0.22	0.074	0.689
	UNIFAC	0.365	0.415	0.175	0.045	0.015	0.225	0.071	0.689
5	Exptl.	0.251	0.171	0.507	0.071	0.019	0.091	0.209	0.681
	UNIQUAC	0.255	0.17	0.5	0.075	0.017	0.093	0.22	0.67
	UNIFAC	0.257	0.166	0.496	0.08	0.014	0.096	0.222	0.668
<i>rmsd</i> value using UNIQUAC = 0.81 <i>rmsd</i> value using UNIFAC = 0.62 <i>rmsd</i> value reported for NRTL = 0.66 (*Chen et al., 2000)									

Table 5.12 Comparison of experimental data for quinary system Hexane(1)-Octane(2)-Benzene(3)-Toluene(4)-TMS(5) with UNIQUAC and UNIFAC predictions.

Tie line		Raffinate phase					Extract phase				
		$x_1'$	$x_2'$	$x_3'$	$x_4'$	$x_5'$	$x_1''$	$x_2''$	$x_3''$	$x_4''$	$x_5''$
1	Exptl.*	0.696	0.118	0.083	0.1	0.004	0.015	0.002	0.055	0.042	0.887
	UNIQUAC	0.695	0.119	0.084	0.101	0.002	0.016	0.001	0.054	0.042	0.887
	UNIFAC	0.692	0.119	0.085	0.101	0.003	0.018	0.001	0.053	0.041	0.886
2	Exptl.	0.232	0.488	0.17	0.098	0.012	0.007	0.009	0.121	0.043	0.821
	UNIQUAC	0.232	0.488	0.175	0.101	0.004	0.007	0.007	0.116	0.039	0.83
	UNIFAC	0.23	0.487	0.179	0.099	0.006	0.008	0.007	0.112	0.042	0.832
3	Exptl.	0.213	0.243	0.396	0.117	0.031	0.019	0.014	0.31	0.067	0.59
	UNIQUAC	0.208	0.237	0.396	0.125	0.035	0.02	0.015	0.308	0.058	0.6
	UNIFAC	0.212	0.244	0.397	0.115	0.031	0.021	0.013	0.309	0.069	0.589
4	Exptl.	0.154	0.13	0.133	0.494	0.088	0.032	0.02	0.112	0.334	0.502
	UNIQUAC	0.153	0.13	0.136	0.496	0.085	0.029	0.017	0.107	0.327	0.519
	UNIFAC	0.159	0.136	0.133	0.49	0.082	0.03	0.016	0.113	0.341	0.501
$rmsd$ value using UNIQUAC = 0.46 $rmsd$ value using UNIFAC = 0.37 $rmsd$ value reported for NRTL = 0.42 (*Chen et. al., 2000 [14])											

Table 5.13 Simultaneous UNIQUAC parameters for Heptane-Toluene-TMS and Heptane-Xylene-TMS at 298.15K

S.N.	Binary pair ij		Initial guess	Regressed parameters	Objective Function	No. of tie lines used	rmsd
	<i>i</i>	<i>j</i>	<i>a<sub>ij</sub></i>	<i>a<sub>ij</sub></i>	$-\ln L$	<i>m</i>	
7	Heptane	Toluene	309.32	303.29	-184.12	10	0.4070
	<u>Heptane</u>	<u>TMS</u>	799.48	641.14			
	Toluene	Heptane	-207.88	-205.85			
	Toluene	TMS	<i>136.04</i>	<i>136.04</i>			
	<u>TMS</u>	<u>Heptane</u>	55.46	48.28			
	TMS	Toluene	-3.56	-3.56			
8	Heptane	Xylene	303.15	281.55	-143.57	10	0.9611
	<u>Heptane</u>	<u>TMS</u>	799.48	641.14			
	Xylene	Heptane	-196.06	-186.97			
	Xylene	TMS	<i>181.20</i>	<i>181.20</i>			
	<u>TMS</u>	<u>Heptane</u>	55.46	48.78			
	TMS	Xylene	-5.14	-5.14			
Total Objective function value $\equiv (-\ln L_1) + (-\ln L_2) = -327.69$							

Table 5.14 Comparison of Predictions using UNIFAC with experimental data for the systems Heptane-Toluene-TMS and Heptane-Xylene-TMS

S. N.	Ternary System	Group assignment	Objective Function	rmsd
7	Heptane Toluene TMS	2 CH <sub>3</sub> , 5 CH <sub>2</sub> 5 ACH, 1 ACCH <sub>3</sub> 1 TMS	-134.84	0.8450
8	Heptane Xylene TMS	2 CH <sub>3</sub> , 5 CH <sub>2</sub> 4 ACH, 2 ACCH <sub>3</sub> 1 TMS	-125.53	1.1516

Table 5.15 Simultaneous UNIQUAC parameters for Heptane-Toluene-TMS and Heptane-Xylene-TMS at 323.15K

S.N.	Binary pair ij		Initial guess	Regressed parameters	Objective Function	No. of tie lines used	rmsd
	<i>i</i>	<i>j</i>	<i>a<sub>ij</sub></i>	<i>a<sub>ij</sub></i>	$-\ln L$	<i>m</i>	
7	Heptane	Toluene	303.29	283.95	-141.18	10	1.0160
	Heptane	TMS	641.14	600.12			
	Toluene	Heptane	-205.85	-210.69			
	Toluene	TMS	136.04	144.56			
	TMS	Heptane	48.28	40.23			
	TMS	Toluene	-3.56	-9.31			
8	Heptane	Xylene	281.55	189.80	-77.87	10	1.5604
	Heptane	TMS	641.14	600.12			
	Xylene	Heptane	-186.97	-161.93			
	Xylene	TMS	181.20	165.98			
	TMS	Heptane	48.78	40.23			
	TMS	Xylene	-5.14	-2.80			
Total Objective function value $\equiv (-\ln L_1) + (-\ln L_2) = -219.06$							

Liquid-liquid equilibrium data for system **Heptane-Toluene-TMS** at temperatures 348.15 K and 373.15 K have been regressed. The LLE data reported by Sorensen and Arlt, 1979 have been used for regression. For initial guess of parameters the parameters obtained at lower temperatures have been used. The parameters after regression are reported in Table 5.16. The *rmsd* values and objective function values are also reported in Table 5.16.

Heptane - Xylene - TMS at 323.15 K  
 Predicted using simultaneously regressed parameters (Table 5.15)

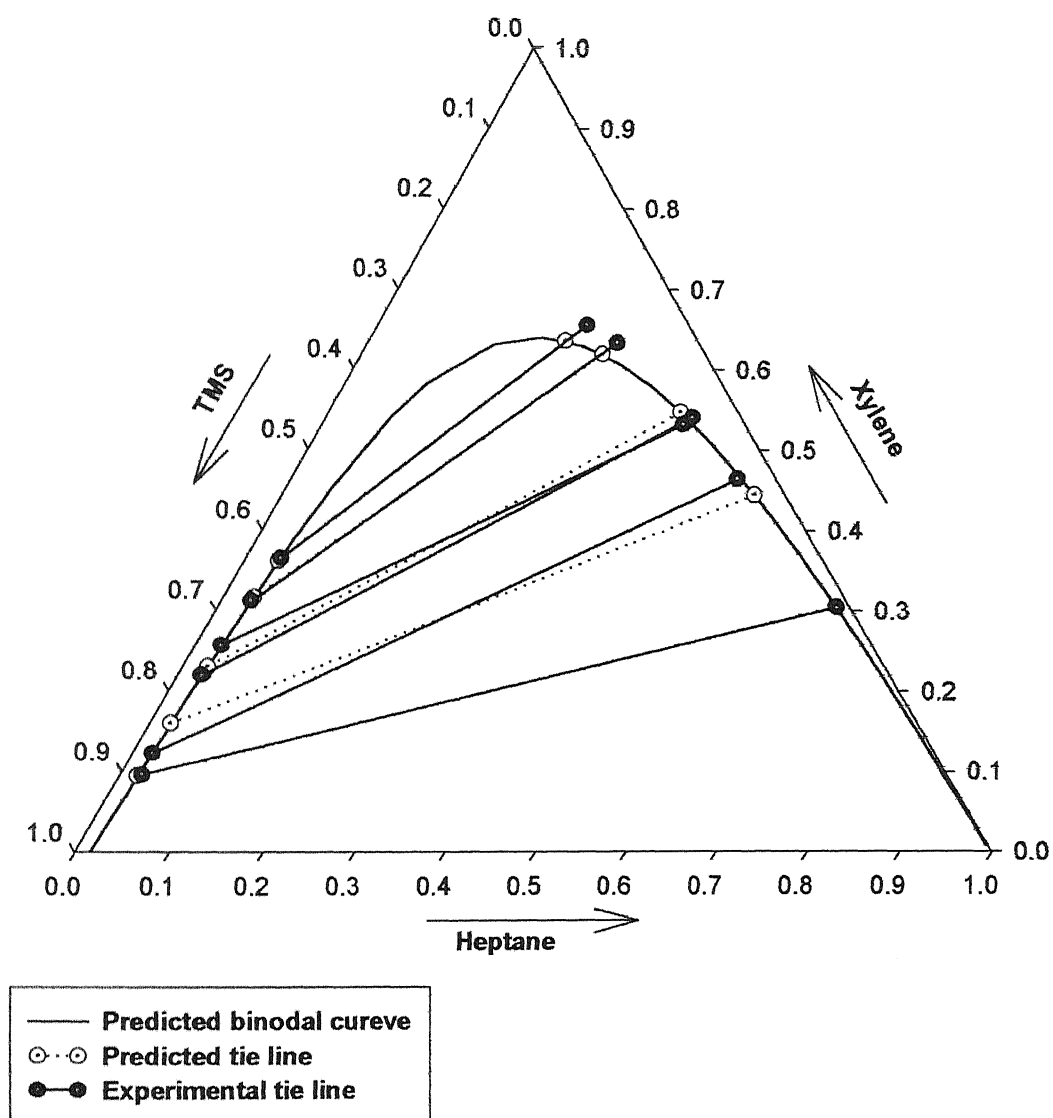


Fig: 5.4 Comparison of LLE Predictions for Heptane - Xylene - TMS  
 ( Worst case,  $rmsd = 1.5604$ )

Table 5.16 UNIQUAC binary interaction parameters for Heptane-Toluene-TMS

Temperature	Binary pair ij		Regressed parameters	Objective Function	No. of tie lines used	rmsd
	<i>i</i>	<i>j</i>	$a_{ij}$	$-\ln L$	<i>m</i>	
298.15	Heptane	Toluene	303.29	-184.12	10	0.4070
	<u>Heptane</u>	<u>TMS</u>	641.14			
	Toluene	Heptane	-205.85			
	Toluene	TMS	<i>136.04</i>			
	<u>TMS</u>	<u>Heptane</u>	48.28			
	TMS	Toluene	<i>-3.56</i>			
323.15	Heptane	Toluene	283.95	-141.18	10	1.0160
	<u>Heptane</u>	<u>TMS</u>	600.12			
	Toluene	Heptane	-210.69			
	Toluene	TMS	144.56			
	<u>TMS</u>	<u>Heptane</u>	40.23			
	TMS	Toluene	<i>-9.31</i>			
348.15	Heptane	Toluene	248.54	-147.85	10	0.8506
	Heptane	TMS	510.47			
	Toluene	Heptane	-220.01			
	Toluene	TMS	164.52			
	TMS	Heptane	29.68			
	TMS	Toluene	<i>-33.73</i>			
373.15	Heptane	Toluene	240.47	-131.44	8	0.7712
	Heptane	TMS	501.53			
	Toluene	Heptane	-205.16			
	Toluene	TMS	98.96			
	TMS	Heptane	26.38			
	TMS	Toluene	25.99			

Adopting a similar procedure UNIQUAC interaction parameters have been regressed for the system **Hexane-Benzene-TMS** at higher temperatures have been estimated. The experimental data have been reported by ( Sorensen and Arlt, 1979 [72]). Table 5.17 gives the regressed parameters for all the four temperatures 298, 323.15, 348.15 and 373.15 K along with the *rmsd* values and objective function values.

Using the similar approach the UNIQUAC interaction parameters for system **Cyclohexane-Benzene-TMS** at different temperatures have been regressed. The LLE data of (Sorensen and Arlt, 1979 [72]) have been used. The regressed parameters are given in Table 5.18. Parameters for pairs Benzene-TMS at different temperatures were kept fixed at their respective values obtained for system Hexane-Benzene-TMS. In Table 5.18 the parameter values shown in italic were kept fixed at their respective values obtained for system Hexane-Benzene-TMS at different temperatures. Table 5.18

also gives the objective function values at the regressed parameters along with the *rmsd* values. For initial guess the parameters obtained for Hexane-Benzene-TMS system, given in Table 5.4 and Table 5.17 have been used.

Table 5.17 UNIQUAC binary interaction parameters for Hexane-Benzene-TMS

Temperature	Binary pair ij		Regressed parameters	Objective Function	No. of tie lines used	rmsd
	<i>i</i>	<i>j</i>	$a_{ij}$	$-\ln L$	<i>m</i>	
298.15K	Hexane	Benzene	-155.47	-160.06	10	0.5698
	Hexane	TMS	799.48			
	Benzene	Hexane	84.61			
	Benzene	TMS	-7.31			
	TMS	Hexane	55.46			
	TMS	Benzene	-11.82			
323.15 K	Hexane	Benzene	-203.52	-161.49	10	0.3312
	Hexane	TMS	715.93			
	Benzene	Hexane	123.67			
	Benzene	TMS	-24.63			
	TMS	Hexane	60.85			
	TMS	Benzene	2.24			
348.15 K	Hexane	Benzene	-243.13	-134.95	9	1.3614
	Hexane	TMS	635.24			
	Benzene	Hexane	193.70			
	Benzene	TMS	-24.51			
	TMS	Hexane	63.13			
	TMS	Benzene	2.73			
373.15 K	Hexane	Benzene	-295.09	-150.62	11	1.2024
	Hexane	TMS	542.49			
	Benzene	Hexane	229.44			
	Benzene	TMS	-24.24			
	TMS	Hexane	67.83			
	TMS	Benzene	2.89			

### 5.2.2 Systems with PC

As shown for the systems involving TMS as solvent that the parameters regressed simultaneously for three-four or more systems can be used for other systems also. Using the same approach as used for TMS, the binary parameters for systems involving PC have been regressed. These values of parameters obtained then used for prediction of multi-component LLE to compare with the experimental data. The

parameters for pairs that are common to systems with TMS as solvent have been kept same. Table 5.19 gives the UNIQUAC interaction parameters regressed simultaneously

Table 5.18 UNIQUAC parameters for Cyclohexane-Benzene-TMS

Temperature	Binary pair ij		Regressed parameters	Objective Function	No. of tie lines	rmsd
	<i>i</i>	<i>j</i>	<i>a<sub>ij</sub></i>	$-\ln L$	<i>m</i>	
298.15 K	Cyclohexane	Benzene	-328.34	-166.01	10	0.689
	Cyclohexane	TMS	617.54			
	Benzene	Cyclohexane	191.26			
	<i>Benzene</i>	<i>TMS</i>	-7.32			
	TMS	Cyclohexane	70.22			
	<i>TMS</i>	<i>Benzene</i>	-11.82			
323.15 K	Cyclohexane	Benzene	-263.83	-168.40	10	0.455
	Cyclohexane	TMS	593.09			
	Benzene	Cyclohexane	213.3157			
	<i>Benzene</i>	<i>TMS</i>	-24.63			
	TMS	Cyclohexane	57.83			
	<i>TMS</i>	<i>Benzene</i>	2.25			
348.15 K	Cyclohexane	Benzene	-296.61	-153.34	9	0.392
	Cyclohexane	TMS	515.26			
	Benzene	Cyclohexane	245.33			
	<i>Benzene</i>	<i>TMS</i>	-24.51			
	TMS	Cyclohexane	54.90			
	<i>TMS</i>	<i>Benzene</i>	2.73			
373.15 K	Cyclohexane	Benzene	-336.93	-121.81	8	0.923
	Cyclohexane	TMS	449.69			
	Benzene	Cyclohexane	257.02			
	<i>Benzene</i>	<i>TMS</i>	-24.69			
	TMS	Cyclohexane	52.15			
	<i>TMS</i>	<i>Benzene</i>	3.22			

for **Heptane-Toluene-PC** and **Heptane-Xylene-PC** at 298.15 K. The experimental LLE data of Salem et al., 1994 and Salem, 1993 have been used for regression. The interaction parameters between the pair Heptane-Toluene and between pair Heptane-Xylene have been kept at the values given in Table 5.13. The values that were kept constant are shown in italic in Table 5.19. Interaction parameters for the pairs shown underlined are common to both the systems. For initial guess the parameters obtained for systems Heptane-Toulene-TMS and Heptane-Xylene-TMS respectively have been used.

Table 5.19 Simultaneous UNIQUAC parameters for Heptane-Toluene-PC and Heptane-Xylene-PC at 298.15K

S.N.	Binary pair ij		Initial guess	Regressed parameters	Objective Function	No. of tie lines used	rmsd
	<i>i</i>	<i>j</i>	$a_{ij}$	$a_{ij}$	$-\ln L$	$m$	
10	Heptane	Toluene	303.29	303.29	-120.84	6	0.1818
	Heptane	PC	836.30	656.58			
	Toluene	Heptane	-205.85	-205.85			
	Toluene	PC	271.79	237.09			
	PC	Heptane	12.64	7.43			
	PC	Toluene	-57.29	-68.52			
11	Heptane	Xylene	281.5	281.50	-90.68	6	0.5888
	Heptane	PC	836.3	656.59			
	Xylene	Heptane	-186.97	-186.97			
	Xylene	PC	633.54	681.35			
	PC	Heptane	12.642	7.43			
	PC	Xylene	-128.82	-160.79			
Total Objective function value $\equiv (-\ln L_1) + (-\ln L_2) = -211.52$							

Table 5.20 UNIFAC group interaction parameters for PC with other main groups

Binary Group Interaction Parameters $a_{ij}$					
i \ j	CH <sub>3</sub>	CH <sub>2</sub>	ACH	ACCH <sub>3</sub>	PC
CH <sub>3</sub>	0	0	-114.8	-115.7	684.82
CH <sub>2</sub>	0	0	-114.8	-115.7	684.82
ACH	156.5	156.5	0	167.0	170.83
ACCH <sub>3</sub>	104.4	104.4	-146.8	0	525.39
PC	-8.42	-8.42	-36.91	-136.62	0
<i>rmsd</i> for system Heptane-Toluene-PC using above parameters = 0.4675					
<i>rmsd</i> for system Heptane-Xylene-PC using above parameters = 0.364806					

The same systems as above have been used to estimate the UNIFAC group interaction parameters. Mutual interaction parameters between groups CH<sub>3</sub>, ACH, and ACCH<sub>3</sub> were directly taken from UNIFAC Table of (Magnussen et. al., 1981 [40]).

Heptane-Toluene-PC at 298.15 K  
Predicted using UNIFAC (Table 5.20)

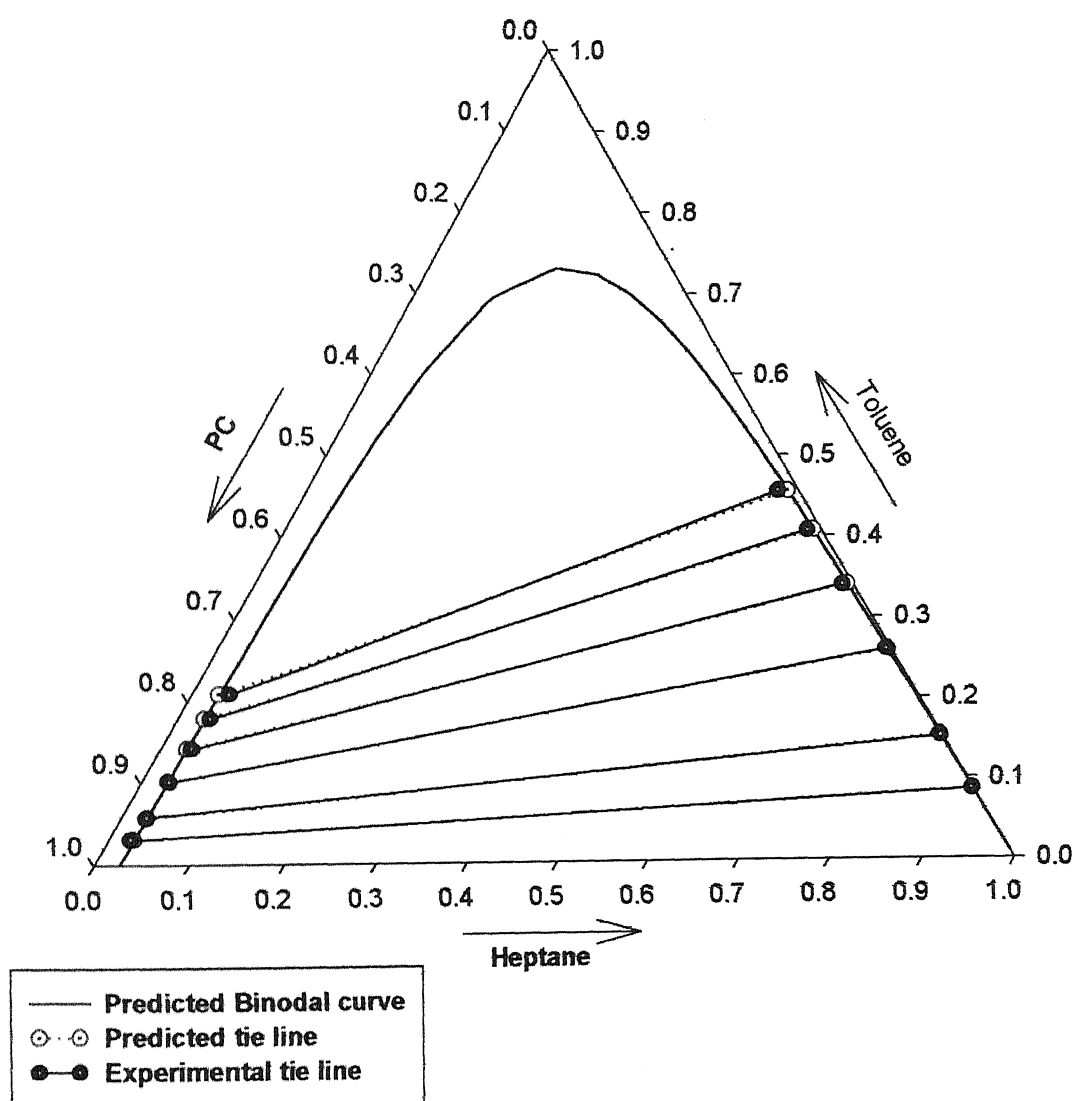


Fig.5.5 LLE Predictions using regressed UNIFAC parameters

The regressed group interaction parameters are reported in the Table 5.20 along with the *rmsd* values. The underlined parameters were kept fixed at those values.

Table 5.21 Comparison of experimental LLE data with predicted for five component system Hexane (1) – Heptane (2) – Toluene (3) – Xylene (4) – PC (5)

Tie Line	Raffinate Phase mole Fractions					
		$x_1^I$	$x_2^I$	$x_3^I$	$x_4^I$	$x_5^I$
1	Experimental	0.482	0.4472	0.0284	0.0405	0.0019
	Our Prediction	0.4837	0.446	0.02817	0.04093	0.0012
	Reported Prediction	0.5001	0.4276	0.0334	0.0386	0.0167
2	Experimental	0.456	0.4152	0.054	0.0742	0.0006
	Our Prediction	0.4567	0.4132	0.05316	0.07517	0.0018
	Reported Prediction	0.4660	0.3985	0.0623	0.0726	0.0006
3	Experimental	0.399	0.366	0.098	0.136	0.001
	Our Prediction	0.3977	0.3607	0.09945	0.13851	0.0036
	Reported Prediction	0.4092	0.3500	0.1096	0.1364	0.0042
4	Experimental	0.383	0.3442	0.1153	0.1572	0.0003
	Our Prediction	0.3815	0.34	0.11514	0.15896	0.0044
	Reported Prediction	0.3853	0.3297	0.1292	0.1572	0.0045
5	Experimental	0.358	0.324	0.132	0.185	0.001
	Our Prediction	0.3543	0.3185	0.13267	0.18878	0.0057
	Reported Prediction	0.3639	0.3114	0.1446	0.1739	0.0058
6	Experimental	0.3401	0.3072	0.1471	0.2032	0.0024
	Our Prediction	0.3376	0.2997	0.15215	0.2036	0.007
	Reported Prediction	0.3408	0.2917	0.1650	0.2032	0.008
Extract Phase mole fractions						
		$x_1^{II}$	$x_2^{II}$	$x_3^{II}$	$x_4^{II}$	$x_5^{II}$
1	Experimental	0.0189	0.0081	0.0099	0.0115	0.9516
	Our Prediction	0.0212	0.0131	0.0103	0.0113	0.9441
	Reported Prediction	0.0107	0.0121	0.0053	0.0123	0.9719
2	Experimental	0.0189	0.0081	0.0188	0.022	0.9322
	Our Prediction	0.0213	0.0129	0.0199	0.0214	0.9245
	Reported Prediction	0.0107	0.0119	0.0104	0.0235	0.914
3	Experimental	0.0212	0.0091	0.0408	0.0449	0.884
	Our Prediction	0.0209	0.0129	0.0391	0.042	0.8851
	Reported Prediction	0.0107	0.0117	0.0199	0.0437	0.8753
4	Experimental	0.0212	0.0101	0.0463	0.0516	0.8708
	Our Prediction	0.021	0.0128	0.0461	0.0493	0.8706
	Reported Prediction	0.0107	0.0116	0.0244	0.0528	0.8643
5	Experimental	0.0212	0.0111	0.0562	0.0659	0.8456
	Our Prediction	0.0208	0.0129	0.0546	0.0605	0.8512
	Reported Prediction	0.0107	0.0115	0.0287	0.0615	0.8523
6	Experimental	0.027	0.0131	0.0714	0.0712	0.8173
	Our Prediction	0.0208	0.0128	0.0639	0.0671	0.8353
	Reported Prediction	0.0107	0.0114	0.0337	0.0712	0.8412

The regressed UNIFAC group interaction parameters have been used to predict a quinary system **Hexane – Heptane – Toluene – Xylene – PC** for which the experimental LLE data at 298.15 K have been reported by ( Salem et. al., 1995 [69]). The predicted mole fractions for this system using UNIFAC parameters reported in Table 5.20, are given in Table 5.21 along with experimental LLE data. Table 5.21 also gives the predicted LLE for this system by ( Salem et. al., 1995 [69] ) using specific UNIQUAC parameters. The predicted mole fractions are in good agreement with experimental data. The *rmsd* value for the predicted compositions reported by (Salem et. al., 1995 [69] ) is 0.876 as compared to 0.41 for this prediction.

### 5.2.3 Systems with N-Formyl-Morpholine

Binary interaction parameters for systems involving N-Formyl-Morpholine (NFM) as solvent have been estimated. Ternary experimental LLE data at 311.15 K for the systems Heptane – Benzene – NFM, Heptane – Toluene – NFM and Heptane – Xylene – NFM have been reported by (Cinotti et. al., 1999 [16]). UNIQUAC binary interaction parameters for these three systems have been regressed simultaneously by adopting the similar approaches as used for TMS and PC systems. The regressed UNIQUAC parameters for these systems are reported in Table 5.23. Objective function values after the regression are also reported in this Table. The *rmsd* values reported in Table 5.23 for three systems, gives an indication of goodness of fit to LLE data. The initial guesses of parameters used are also reported in Table 5.23.

The same ternary systems as used for UNIQUAC parameter estimation have been used to estimate the UNIFAC group interaction parameters. Group interaction parameters for NFM with three main groups CH<sub>3</sub>, ACH, and ACCH<sub>3</sub> have been regressed. The mutual interaction parameters between these three groups have been kept fixed at their respective values given by (Magnussen et. al., 1981 [40] ). The regressed parameters along with the *rmsd* values are reported in Table 5.22. The objective function values after regression for three systems have also been reported in Table 5.22. The binary pairs common for the three ternary systems used are underlined in Table 5.23. The *rmsd* values obtained for UNIFAC are comparable with that of UNIQUAC. The total objective function value for the three ternary systems for UNIFAC is –193.06 as compared to –204.65 for UNIQUAC.

Table 5.22 UNIFAC group interaction parameters for NFM with other main groups

Binary Group Interaction Parameters $a_{ij}$					
$i \backslash j$	CH <sub>3</sub>	CH <sub>2</sub>	ACH	ACCH <sub>3</sub>	NFM
CH <sub>3</sub>	0	0	-114.8	-115.7	379.13
CH <sub>2</sub>	0	0	-114.8	-115.7	379.13
ACH	156.5	156.5	0	167.0	-2.05
ACCH <sub>3</sub>	104.4	104.4	-146.8	0	113.61
NFM	38.18	38.18	78.67	35.17	0
<i>rmsd</i> and objective function for system Heptane-Benzene-NFM = 0.6367, -60.33					
<i>rmsd</i> and objective function for system Heptane-Toluene-NFM = 0.7258, -56.149					
<i>rmsd</i> and objective function for system Heptane-Xylene-NFM = 0.2854, -76.5832					

Table 5.23 Simultaneous UNIQUAC parameters for Heptane-Benzene-NFM, Heptane-Toluene-NFM and Heptane-Xylene-NFM at 311.5

S.N.	Binary pair ij		Initial guess	Regressed parameters	Objective Function	No. of tie lines used	rmsd
	<i>i</i>	<i>j</i>	<i>a<sub>ij</sub></i>	<i>a<sub>ij</sub></i>	$-\ln L$	<i>m</i>	
12	Heptane	Benzene	303.29	111.59	-61.86	4	0.5399
	<u>Heptane</u>	<u>NFM</u>	656.59	363.60			
	Benzene	Heptane	-205.85	-153.63			
	Benzene	NFM	237.08	-17.96			
	<u>NFM</u>	<u>Heptane</u>	7.43	46.55			
	NFM	Benzene	-68.52	5.10			
13	Heptane	Toluene	303.29	293.16	-63.06	4	0.5426
	<u>Heptane</u>	<u>NFM</u>	656.59	363.59			
	Toluene	Heptane	-205.85	-208.34			
	Toluene	NFM	237.08	313.37			
	<u>NFM</u>	<u>Heptane</u>	7.43	46.55			
	NFM	Toluene	-68.56	-130.58			
14	Heptane	Xylene	303.29	233.84	-79.70	4	0.2362
	<u>Heptane</u>	<u>NFM</u>	656.59	363.59			
	Xylene	Heptane	-205.85	-173.54			
	Xylene	NFM	237.08	112.94			
	<u>NFM</u>	<u>Heptane</u>	7.43	46.55			
	NFM	Xylene	-68.52	8.36			
Total Objective function value $\equiv (-\ln L_1) + (-\ln L_2) + (-\ln L_3) = -204.65$							

### 5.2.4 Systems with Dimethyl-Sulfoxide (DMSO)

Ternary experimental LLE for system **Hexane – Benzene – DMSO** at three different temperatures have been reported by (Cassell et. al., 1989 [11]). The LLE data at 298.15 K for Hexane – Benzene – DMSO and Heptane – Toluene – DMSO have been used to estimate the UNIQUAC binary interaction parameters. Ternary LLE data for system **Heptane – Toluene – DMSO** have been reported by (Sorensen and Arlt, 1979 [72]). The estimated UNIQUAC parameters for Hexane – Benzene – DMSO at 298.15 K and 323.15 K are given in Table 5.24 along with the initial guesses of parameters used. The objective function and *rmsd* values are also reported in Table 5.24. The *rmsd* values using the reported parameters by (Cassell et. al., 1989 [11]) are also given in Table 5.24.

Table 5.24 Estimated UNIQUAC interaction parameters for system Hexane – Benzene – DMSO

Temp.	Binary pair ij		Initial guess	Regressed parameters	Objective Function	No. of tie lines	rmsd
	<i>i</i>	<i>j</i>	$a_{ij}$	$a_{ij}$	$-\ln L$	$m$	
298.15	Hexane	Benzene	-155.45	-155.47	-112.05	7	0.6084
	Hexane	DMSO	544.64	648.80			
	Benzene	Hexane	84.61	84.61			
	Benzene	DMSO	136.23	129.69			
	DMSO	Hexane	58.75	64.62			
	DMSO	Benzene	-161.71	-146.25			
323.15	Hexane	Benzene	-203.52	-203.52	-114.19	6	0.4772
	Hexane	DMSO	542.42	544.63			
	Benzene	Hexane	123.52	123.55			
	Benzene	DMSO	133.52	136.23			
	DMSO	Hexane	61.08	58.75			
	DMSO	Benzene	-151.57	-161.71			
<i>rmsd</i> using the UNIQUAC reported* parameters at 298.15 = 1.578							
<i>rmsd</i> using the NRTL reported* parameters at 298.15 = 1.624							
<i>rmsd</i> using the UNIQUAC reported* parameters at 323.15 = 0.9472							
<i>rmsd</i> using the NRTL reported* parameters at 323.15 = 1.0234							
* Reported by ( Cassell et. al., 1989 [11] )							

UNIQUAC parameters for system Heptane – Toluene – DMSO at 298.15 K have been estimated and reported in Table 5.25. The *rmsd* values and objective

function values are also reported in Table 5.25 for this system. The interaction parameters shown in *italic* were kept fixed at the values, which have been regressed earlier. Regressed parameters for Heptane – Toluene – DMSO system, were taken as initial guesses.

Table 5.25 Estimated UNIQUAC parameters for Heptane – Toluene – DMSO at 298.15 K.

Temp.	Binary pair ij		Initial guess	Regressed parameters	Objective Function	No. of tie lines	rmsd
	<i>i</i>	<i>j</i>	$a_{ij}$	$a_{ij}$	$-\ln L$	<i>m</i>	
298.15	<i>Heptane</i>	<i>Toluene</i>	303.29	303.29	-97.62	8	0.6075
	Heptane	DMSO	641.14	540.21			
	<i>Toluene</i>	<i>Heptane</i>	-205.85	-205.85			
	Toluene	DMSO	136.04	554.33			
	DMSO	Heptane	48.78	95.80			
	DMSO	Toluene	-3.55	-147.53			

Table 5.26 Simultaneous UNIFAC group interaction parameters for Hexane-Benzene-DMSO and Heptane-Toluene-DMSO at 298.15K

Binary Group Interaction Parameters $a_{ij}$					
$\begin{matrix} j \\ i \end{matrix}$	CH <sub>3</sub>	CH <sub>2</sub>	ACH	ACCH <sub>3</sub>	DMSO
CH <sub>3</sub>	0	0	-114.8	-115.7	722.11
CH <sub>2</sub>	0	0	-114.8	-115.7	722.11
ACH	156.5	156.5	0	167.0	153.99
ACCH <sub>3</sub>	104.4	104.4	-146.8	0	188.46
DMSO	45.93	45.93	-44.48	72.15	0
rmsd and objective function for system Hexane-Benzene-DMSO = 0.6183, -99.4046					
rmsd and objective function for system Heptane-Toluene-DMSO = 0.9452, -88.1820					

UNIFAC group binary interaction parameters for the groups CH<sub>3</sub>, ACH, and ACCH<sub>3</sub> with DMSO have been regressed using the ternary LLE data for Hexane – Benzene – DMSO and Heptane – Toluene – DMSO. The regressed parameters are

given in Table 5.26. Mutual interaction parameters between the groups  $\text{CH}_3$ ,  $\text{ACH}$ , and  $\text{ACCH}_3$  were kept fix at their respective values as given by (Magnussen et. al., 1981 [40] ). The objective function and *rmsd* values are also reported in Table 5.26. The prediction using UNIFAC are comparable with UNIQUAC.

### 5.2.5 Systems with Triethylene-Glycol (TREG)

Liquid – Liquid equilibrium data for **Hexane – Benzene – TREG** have been reported by ( Sorensen and Arlt, 1979 [72] ). LLE data at 293.15 K, 313.15 K and 333.15 K temperatures have been reported. These data have been used to estimate the binary interaction parameters for the UNIQUAC model. For parameters estimation same procedure has been used, as used for other systems. The results of parameter estimations are given in Table 5.27. For initial guesses of parameters the activity difference objective function of equation (4.3) have been used. The LLE data at 293.15 K have been used to minimize the activity difference objective function. The parameters obtained then were used as initial guess for objective function of equation (4.12). For parameter estimation at 313.15 K and 333.15 K the parameters obtained at lower temperatures have been used as initial guesses as shown in Table 5.27. The *rmsd* values and objective functions after regression are also reported in Table 5.27.

### 5.2.6 Systems with N-Methyl-Pyrrolidone

Ternary Liquid – Liquid equilibrium data for system Heptane – Toluene – NMP have been reported by (Ferreira et. al., 1984 [24]). LLE data at temperature 298.15 K have been used to regress the binary interaction parameters for UNIQUAC. The regressed parameters are reported in Table 5.28. For initial guess of parameters the activity difference objective function of equation (4.3) have been minimized. The parameters obtained using activity difference objective function were then used to minimize the objective function of equation (4.12). The initial guess of parameters is also reported in Table 5.28. The *rmsd* values are also reported in Table 5.28 along with the objective function value.

UNIFAC group interaction parameters for the main groups  $\text{CH}_3$ ,  $\text{ACH}$ , and  $\text{ACCH}_3$  with NMP have been estimated using the Heptane – Toluene – NMP at 298.15 K. LLE Data reported by (Ferreira et. al., 1984 [24]) have been used for this. The UNIFAC group interaction parameters between NMP and other main groups are reported in Table 5.28. The mutual interaction parameters between the groups  $\text{CH}_3$ ,

ACH, and ACCH<sub>3</sub> were kept fix at their respective values as given by Magnussen et al., 1981.

### 5.2.7 Systems with Dimethyl-Formamide (DMF)

Ternary LLE data for the system **cyclohexane – Benzene – DMF** at 303.15 K have been reported by Sorenson and Arlt, 1979. UNIQUAC binary interaction parameters for system Cyclohexane (CY) – Benzene - DMF have been estimated using these data. The estimated UNIQUAC parameters for this system are reported in Table 5.29. The *rmsd* values and objective function values are also given in Table 5.29. Due to unavailability of sufficient data for this system, UNIFAC parameters have not been estimated.

Table 5.27 Estimated UNIQUAC interaction parameters for system Hexane – Benzene – TREG

Temp.	Binary pair ij		Initial guess	Regressed parameters	Objective Function	No. of tie lines	rmsd
	<i>i</i>	<i>j</i>	$a_{ij}$	$a_{ij}$	$-\ln L$	<i>m</i>	
293.15	Hexane	Benzene	706.78	262.23	-77.70	4	0.2818
	Hexane	TREG	805.26	443.59			
	Benzene	Hexane	-299.73	-161.23			
	Benzene	TREG	346.03	336.61			
	TREG	Hexane	68.68	81.65			
	TREG	Benzene	-103.28	-77.48			
313.15	Hexane	Benzene	262.23	233.92	-77.25	4	0.2690
	Hexane	TREG	443.59	432.64			
	Benzene	Hexane	-161.23	-145.64			
	Benzene	TREG	336.61	256.63			
	TREG	Hexane	81.65	76.16			
	TREG	Benzene	-77.48	-36.33			
333.15	Hexane	Benzene	233.92	302.73	-74.98	4	0.3147
	Hexane	TREG	432.64	365.82			
	Benzene	Hexane	-145.64	-183.29			
	Benzene	TREG	256.63	246.01			
	TREG	Hexane	76.16	103.23			
	TREG	Benzene	-36.33	-29.17			

Table 5.28 UNIQUAC binary interaction parameters for the system Heptane – Toluene – NMP at 298.15 K

Temp.	Binary pair ij		Initial guess	Regressed parameters	Objective Function	No. of tie lines	rmsd
	<i>i</i>	<i>j</i>	$a_{ij}$	$a_{ij}$	$-\ln L$	<i>m</i>	
298.15	Heptane	Toluene	303.29	303.29	-97.62	8	0.6075
	Heptane	NMP	641.14	540.21			
	Toluene	Heptane	-205.85	-205.85			
	Toluene	NMP	136.04	554.33			
	NMP	Heptane	48.78	95.80			
	NMP	Toluene	-3.56	-147.53			

Table 5.29 UNIQUAC binary interaction parameters for the system Cyclohexane – Benzene – DMF at 298.15 K

Temp.	Binary pair ij		Regressed parameters	Objective Function	No. of tie lines	rmsd
	<i>i</i>	<i>j</i>	$a_{ij}$	$-\ln L$	<i>m</i>	
298.15	Cyclohexane	Benzene	354.79	-53.59	3	1.170
	Cyclohexane	DMF	315.89			
	Benzene	Heptane	-228.99			
	Benzene	DMF	105.91			
	DMF	Cyclohexane	3.23			
	DMF	Benzene	-35.01			

Table 5.30 UNIFAC group binary interaction parameters for NMP

Binary Group Interaction Parameters $a_{ij}$					
<i>i</i> \ <i>j</i>	CH <sub>3</sub>	CH <sub>2</sub>	ACH	ACCH <sub>3</sub>	NMP
CH <sub>3</sub>	0	0	-114.8	-115.7	224.19
CH <sub>2</sub>	0	0	-114.8	-115.7	224.19
ACH	156.5	156.5	0	167.0	-130.68
ACCH <sub>3</sub>	104.4	104.4	-146.8	0	29.05
NMP	19.78	19.78	76.52	144.64	0
$rmsd = 1.1003$					
objective function = -154.8828					

## 5.2.8 System with DEG

Ternary LLE data for the system Heptane – Toluene – DEG have been reported by Sorensen and Arlt, 1979. These data have been used to estimate the UNIQUAC binary parameters. The regressed parameters are given in Table 5.31 along with initial guesses used. Parameters for the pair Heptane – Toluene were kept fix at the values obtained for other systems and shown italic in Table 5.31. The *rmsd* and objective function values are also reported in Table 5.31.

Table 5.31 UNIQUAC binary interaction parameters for the system Heptane – Toluene – DEG at 298.15 K

Temp.	Binary pair ij		Initial guess	Regressed parameters	Objective Function	No. of tie lines	rmsd
	<i>i</i>	<i>j</i>	<i>a<sub>ij</sub></i>	<i>a<sub>ij</sub></i>	$-\ln L$	<i>m</i>	
298.15	Heptane	Toluene	<i>303.29</i>	<i>303.29</i>	-159.70	8	0.1699
	Heptane	DEG	641.14	948.82			
	Toluene	Heptane	-205.85	-205.85			
	Toluene	DEG	136.04	439.13			
	DEG	Heptane	48.79	-0.27			
	DEG	Toluene	-3.55	-36.85			

## 5.3 Effect of Temperature on binary interaction parameters

The effect of temperature on the interaction parameters for UNIQUAC has also been considered. To incorporate the effect of temperature on the binary interaction parameters, the parameters for UNIQUAC has been considered temperature dependent, as it has been used for UNIFAC parameters. The variation of parameters with temperature is shown in Figures 5.6 to 5.10. The variation of parameters for Hexane – Benzene – TMS with temperature is shown in Figure 5.6. The parameters are reported in Table 5.17.

Similarly, the variation of parameters for systems Heptane – Toluene – TMS, Cyclohexane – Benzene – TMS and Hexane – Benzene – DMSO with temperature is given in Figure 5.7, Figure 5.8, and Figure 5.9 respectively. The parameters are

reported in Table 5.16, Table 5.18, and Table 5.24 respectively. The temperature dependency of UNIQUAC parameters considered here is given by equation (5.2)

$$a_{ij} = a_{ij}^0 + a_{ij}^1(T) \quad (4.21)$$

Therefore a linear variation of parameters with temperature has been assumed. The regression procedure has been modified to consider this temperature dependence of parameters. LLE data for the same systems at different temperature have been used. For example for system (1), the data at temperatures 298.15 K, 323.15 K, 348.15 K, and 373.15 K have been used to regress simultaneously the temperature dependent parameters.

### Variation of UNIQUAC parameters with temperature

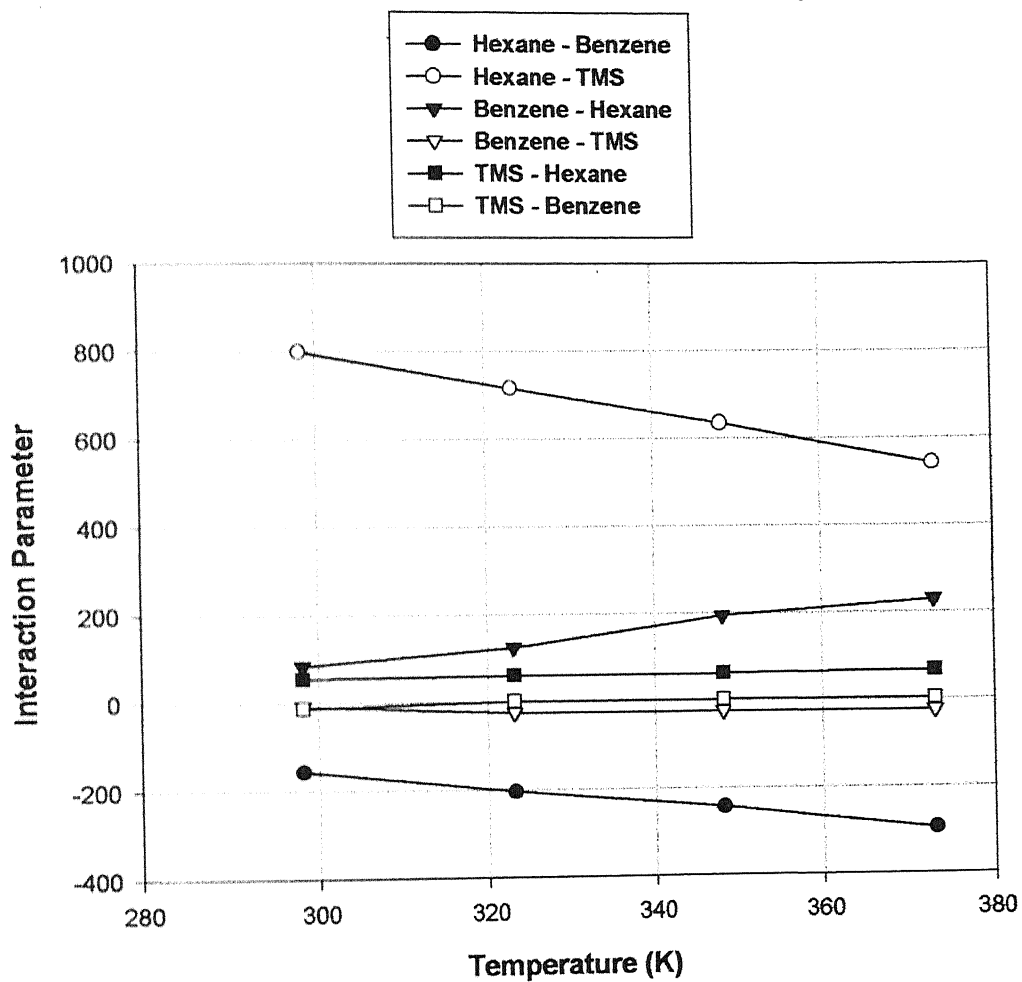


Fig. 5.6 Variation of Binary Interaction Parameters with Temperature  
Hexane - Benzene - TMS

# Variation of UNIQUAC parameters with Temperature

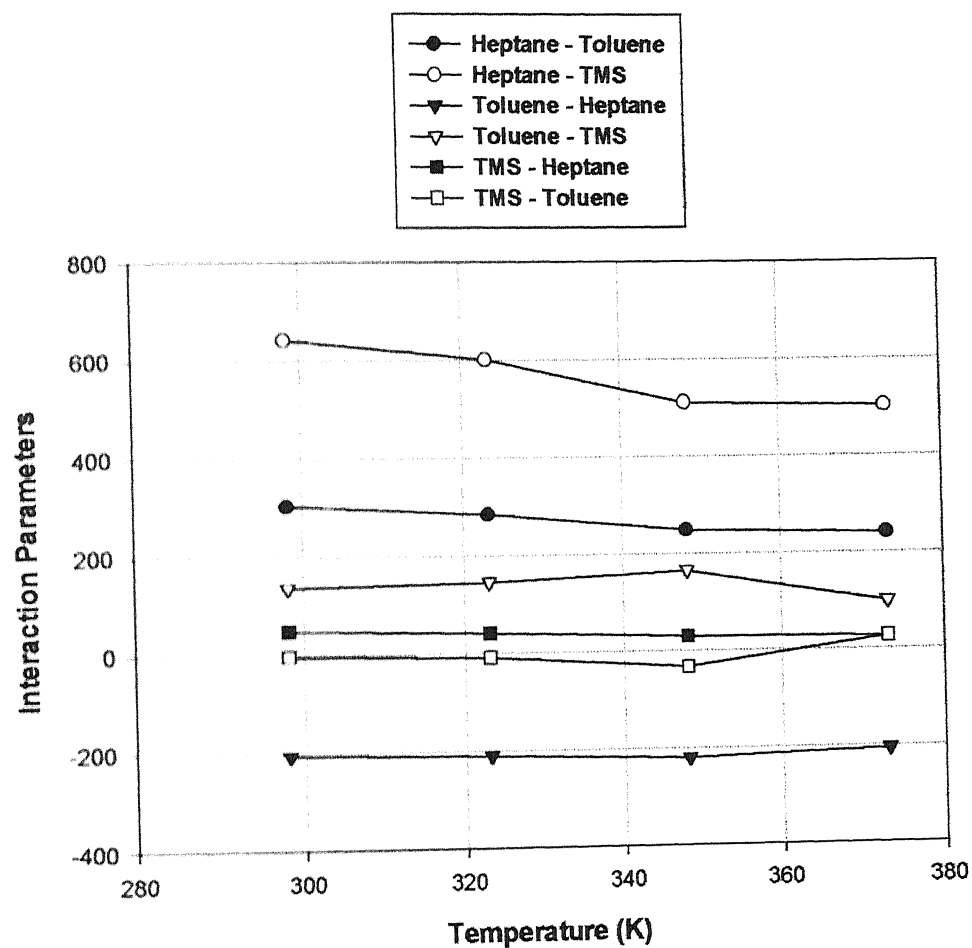


Fig: 5.7 Variation of Binary Interaction Parameters with Temperature  
Heptane - Toluene - TMS

### Variation of UNIQUAC Parameters with Temperature

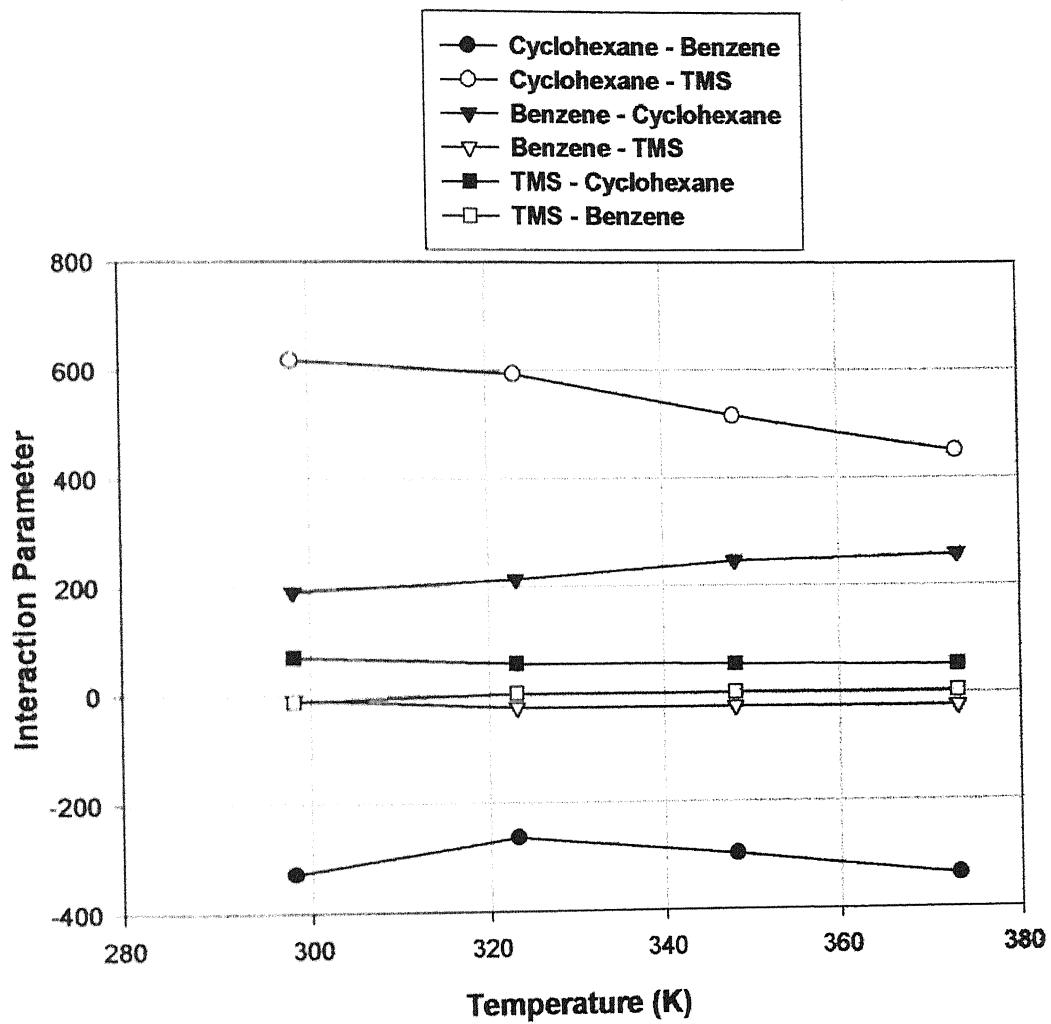


Fig. 5.8 Variation of binary interaction parameters with temperature  
For Cyclohexane - Benzene - TMS

# Variation of UNIQUAC parameters with Temperature

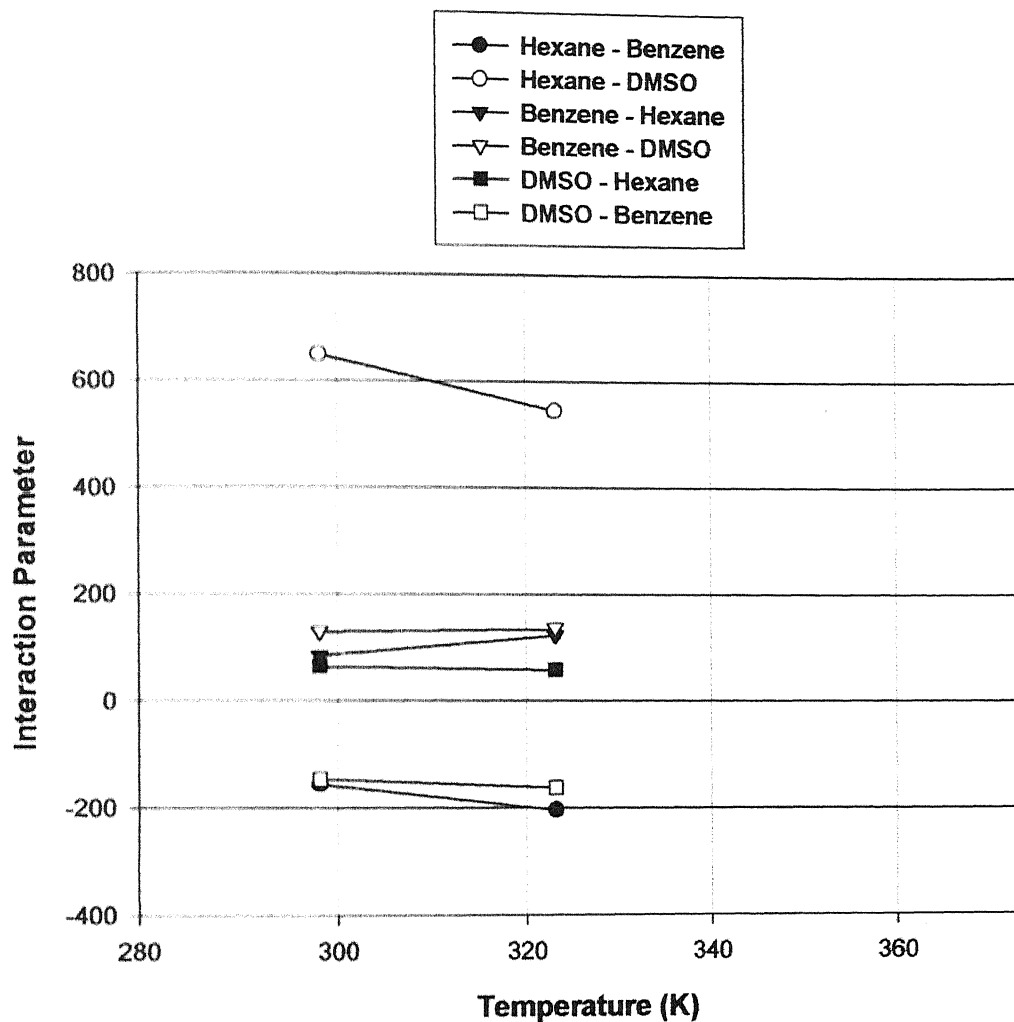


Fig:5.9 Variation of Binary Interaction Parameters with Temperature  
Hexane - Benzene - DMSO

## Chapter 6

### Solvent Performance Evaluation Results

#### 6.1 Interchange Energies

As discussed in chapter 3 the interchange energy given by equation (3.6) and (3.7), gives an indication of solvent performance. These energies are estimated using the UNIFAC group parameters. The estimated UNIFAC group parameters have been used for this purpose. Table 6.1 gives the interchange energies calculated for five solvents using the parameters reported in chapter 5.

Table 6.1 Interchange Energies of Solvents with CH<sub>2</sub> and ACH groups

Solvent	Interchange Energies (K)	
	CH <sub>2</sub>	ACH
TMS	358.92	45.32
DMSO	495.96	56.95
NMP	122.10	-27.01
PC	338.29	66.93
NFM	208.65	38.31

It can be observed from the Table 6.1 that the difference in interchange energies of TMS with CH<sub>2</sub> and ACH groups, which represents nonaromatic and aromatic components respectively, is very large. Hence TMS will have a large selectivity towards aromatics. Similar behavior is observed for DMSO. The differences in interchange energies for other solvents are also appreciable, although lower than that of TMS and DMSO.

#### 6.1 Performance of Solvents for a Single Stage Extraction

Performance of different solvents for aromatic extraction has been evaluated. The UNIQUAC activity coefficient model parameters obtained in previous chapter have been used to estimate the selectivity, solvent power and performance index. To evaluate the performance of solvents the feed has been assumed to be of one aromatic key component and one non-aromatic key component. Selectivity and solvent power of solvents has been estimated for a single equilibrium extraction stage. For a particular feed composition, temperature and solvent to feed ratio the phase equilibrium compositions has been predicted using the UNIQUAC model with estimated parameters. For phase equilibria prediction the equations (4.16), (4.17) and (4.18) has

been solved simultaneously. For this instead of taking mid point ( $z_1, z_2$ ) of tie lines, the feed composition has been used in equation (4.18), because the predicted tie line should pass through the feed point.

Using the above procedure the selectivity, solvent capacity and performance indexes have been estimated. For a **feed of 20 % aromatics** and for a **solvent to feed ratio of 1.0**, the selectivity and solvent capacity have been estimated at 298.15 K and are given in Table 6.2. The aromatic - nonaromatic pair considered here is either the Hexane – Benzene or Heptane – Toluene, based on the availability of LLE data

Table 6.2 Performance of Solvents for Single Stage Extraction

Solvent	Selectivity	Capacity	PI
TMS	34.57	0.711	24.58
DMSO	22.25	0.774	17.24
TREG	21.67	0.533	11.56
NFM	12.44	0.541	6.73
PC	12.92	0.392	5.07
NMP	3.34	1.078	3.69514
DEG	7.22	0.133	0.967

The variation of selectivity, solvent capacity and performance index with aromatic content of feed, solvent to feed ratio, and temperature have also been estimated. Figure 6.1 gives the variation of selectivity with aromatic content of the feed for different solvents for a solvent to feed ratio of 1.0 and temperature of 298.15 K. It has been observed that the selectivity for all solvents decreases with increasing aromatic content of feed. Selectivity of TMS has been found greatest among the solvents considered here. Pure NMP, because of its small two phase region, cannot be used for high aromatic content feed. Figure 6.2 gives the variation of solvent capacity with aromatic content of feed. The solvent capacity of DMF is found to be greatest as compared to other solvents. Solvent capacity of NMP is higher than the other solvents for aromatic content range of feed. The variation of performance index, based on the selectivity and solvent capacity, with aromatic content of feed is shown in Figure 6.3.

The effect of solvent to feed ratio on the solvent performance can be observed by considering a feed with 50 mole % aromatics at 298.15 K temperature. The effect of solvent to feed ratio on the selectivity of different solvents is shown in Figure 6.4. For almost all solvents the selectivity increases with solvent to feed ratio, except for DEG. The selectivity of DEG does not change appreciably with changing solvent to feed ratio. The effect of solvent to feed ratio on solvent capacity is shown in Figure 6.5. The solvent capacity of NMP is found to be highest. The capacity does not change appreciably for almost all solvents. Similarly the variation of performance index with solvent to feed ratio is shown in Figure 6.6. The performance of each solvent increases with solvent to feed ratio, as may be expected.

Effect of temperature on performance of solvents has also been estimated. Figure 6.7 gives the effect of temperature on selectivity of different solvents towards aromatics for a feed containing 50 mole % aromatics and a solvent to feed ratio of 1.0. Selectivity of all the solvents decreases with temperature. Figure 6.8 provides the variation of performance index with temperature. The performance index decreases with temperature, except for PC, which shows a different behaviour than other solvents. Therefore the propylene carbonate seems have better extraction properties at higher temperatures.

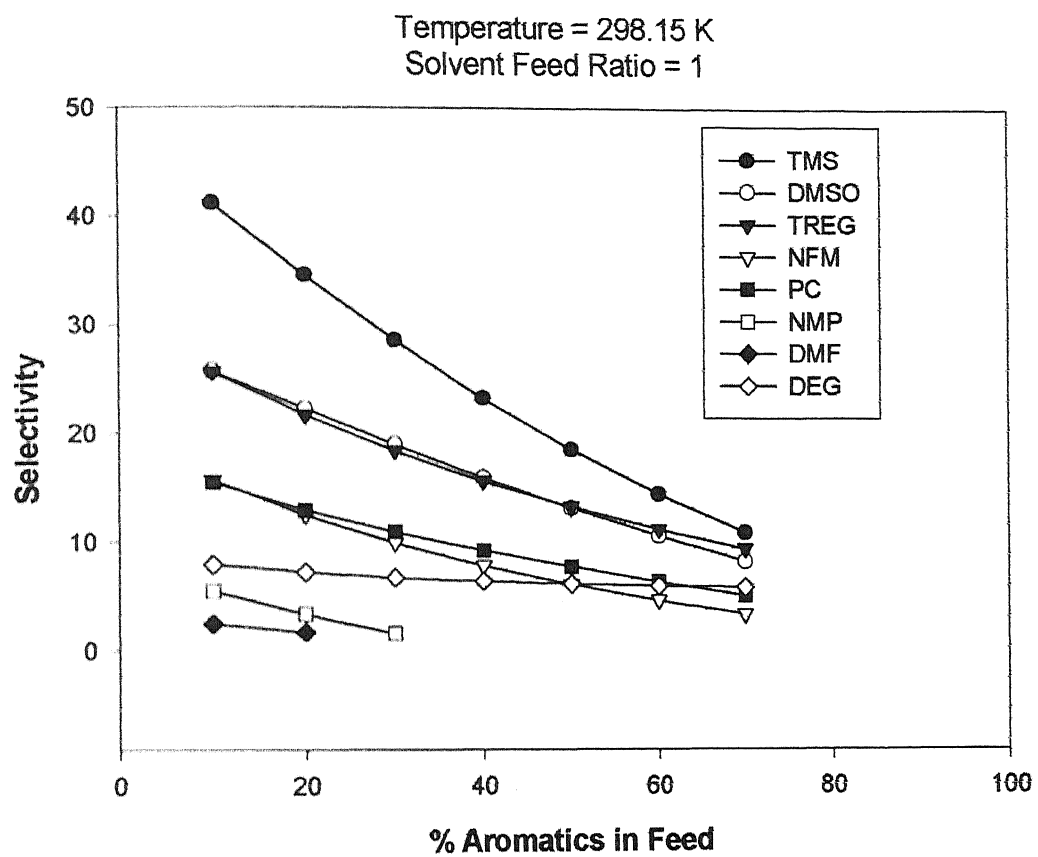


Fig. 6.1 Variation of Selectivity with % Aromatics in Feed

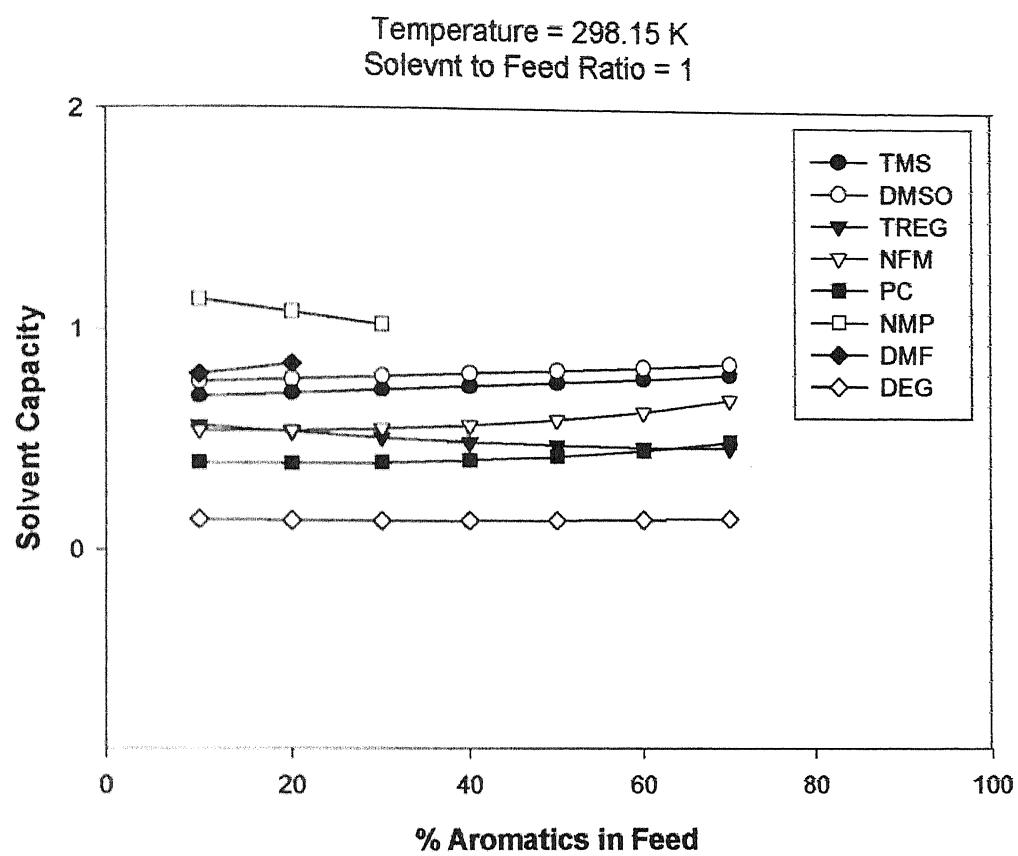


Fig. 6.2 Variation of Solvent Capacity with % Aromatics in Feed

Temperature = 298.15 K  
Solevnt to Feed Ratio = 1

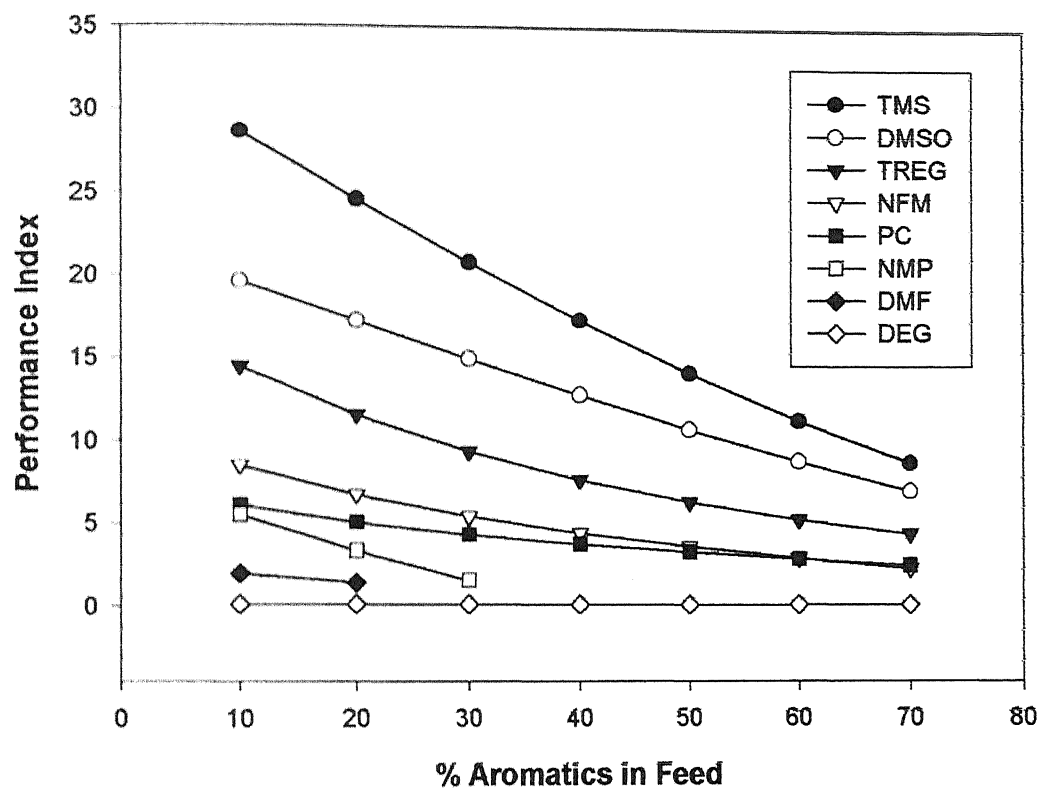


Fig. 6.3 Variation of Performance Index with % Aromatics in Feed

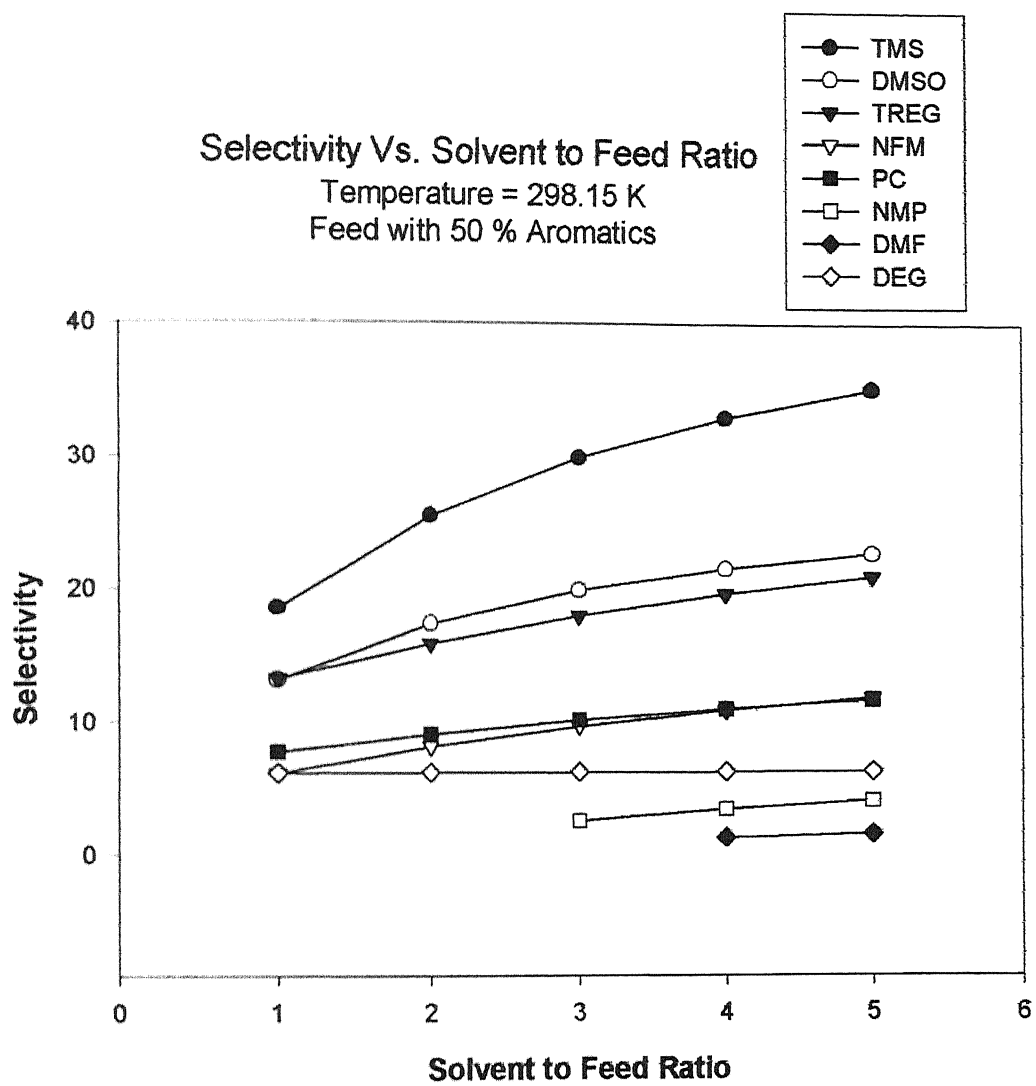


Fig: 6.4 Variation of Selectivity with Solvent to Feed Ratio

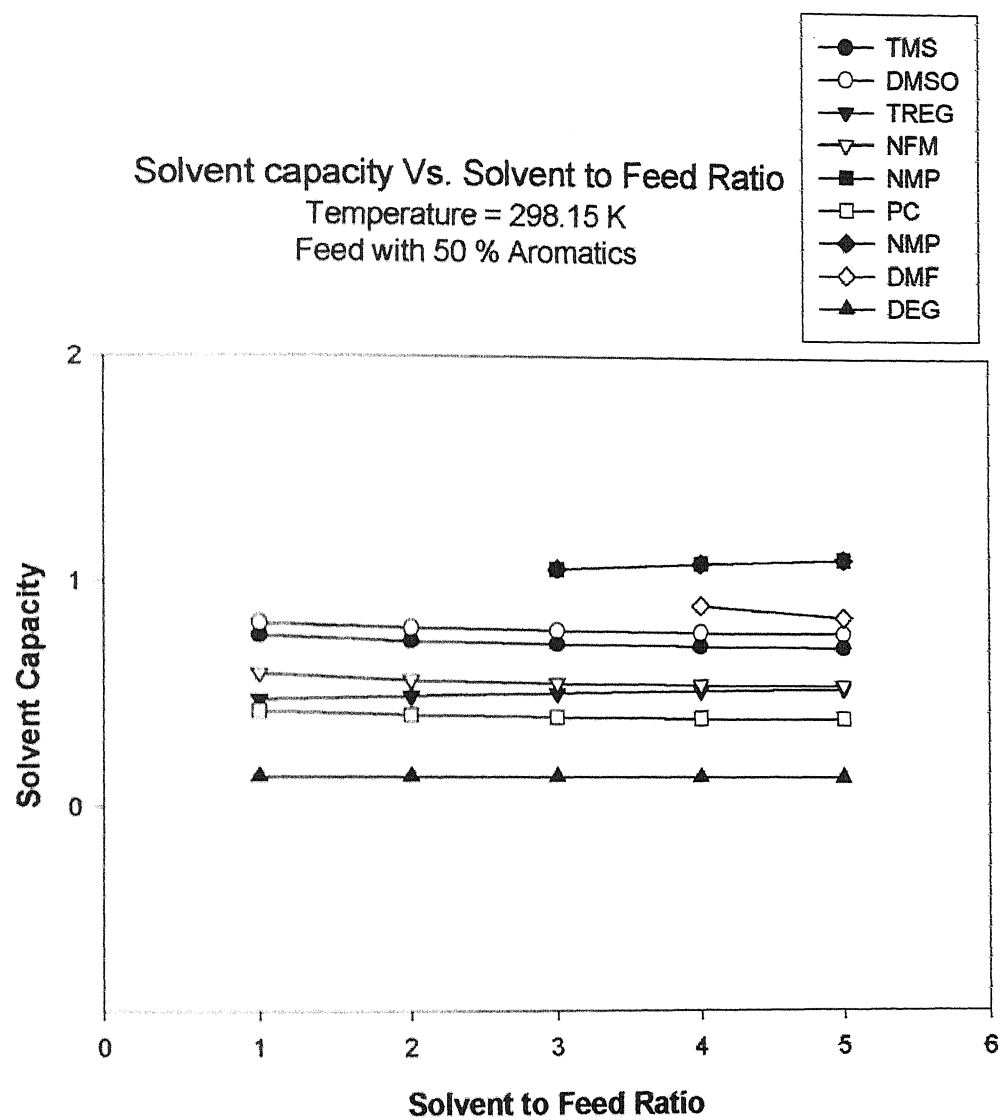


Fig:6.5 Variation of Solvent Capacity with Solvent to Feed Ratio

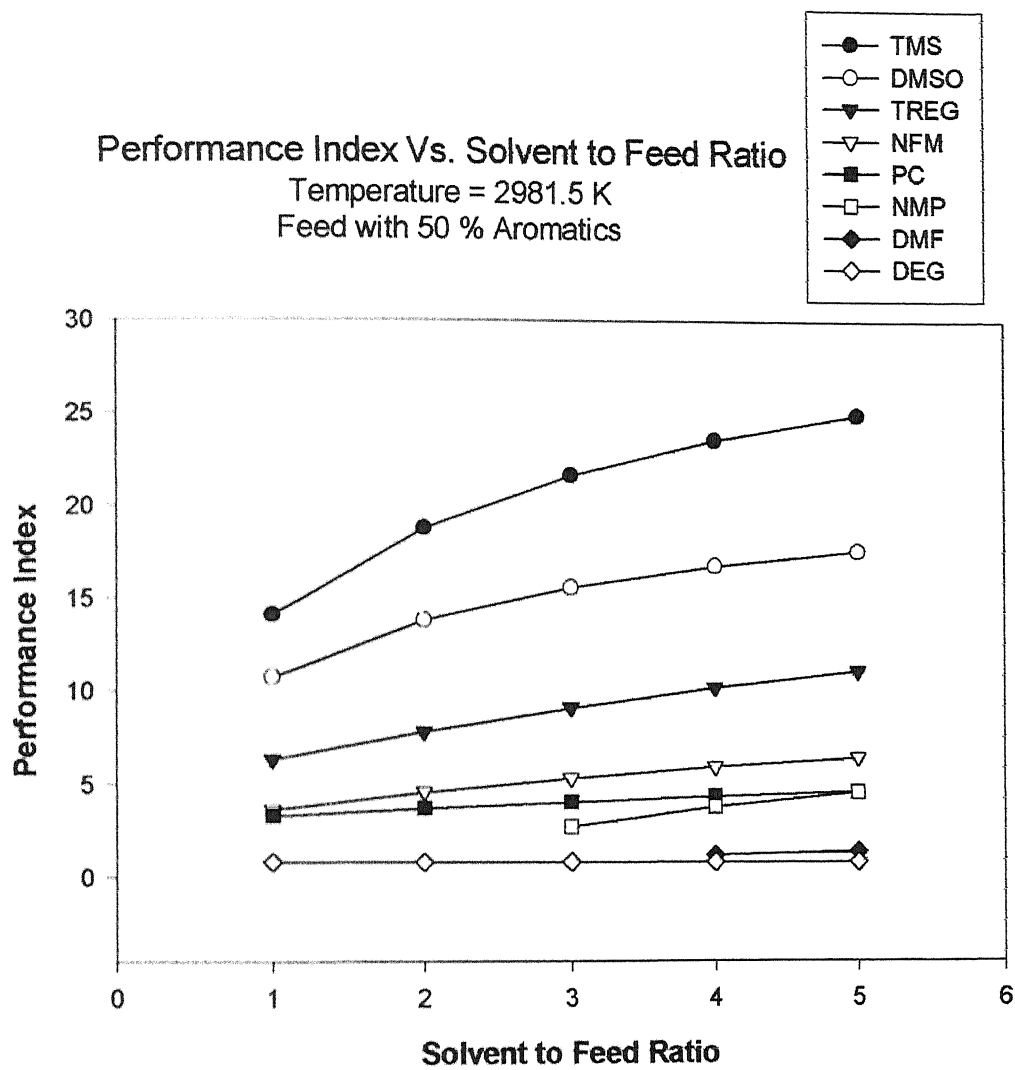


Fig.6.6 Variation of Performance Index with Temperature

### Selectivity Vs. Temperature

Solvent to Feed Ratio = 1

Feed with 50 % Aromatics

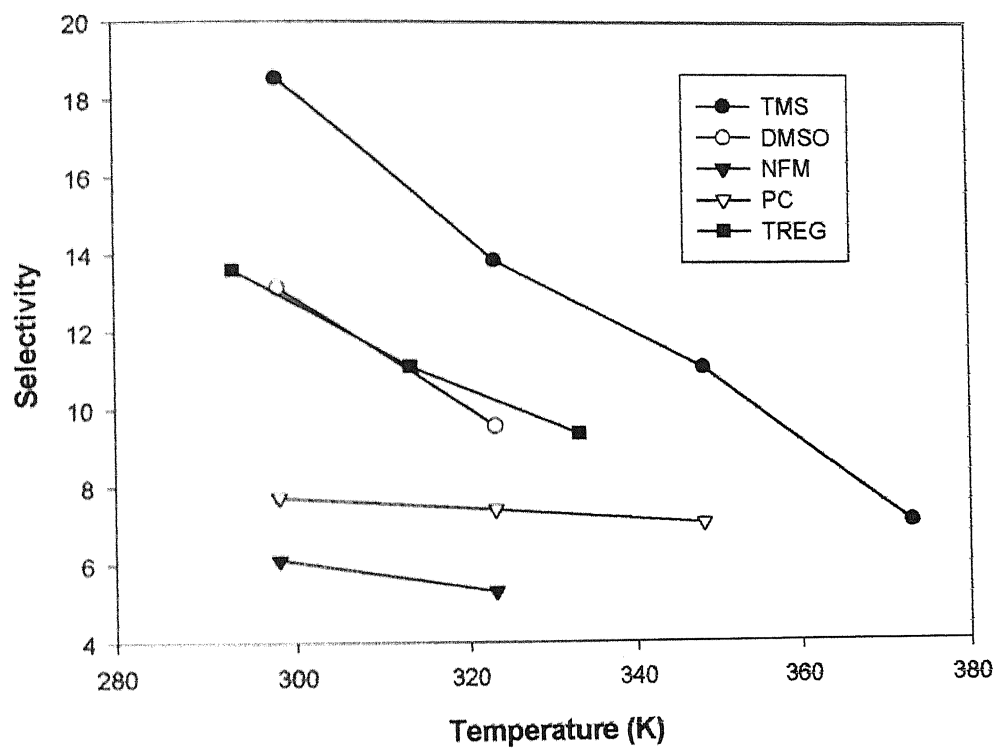


Fig: 6.7 Variation of Selectivity with Temperature

Performance Index Vs. Temperature  
Solvent to Feed Ratio = 1  
Feed with 50 % Aromatics

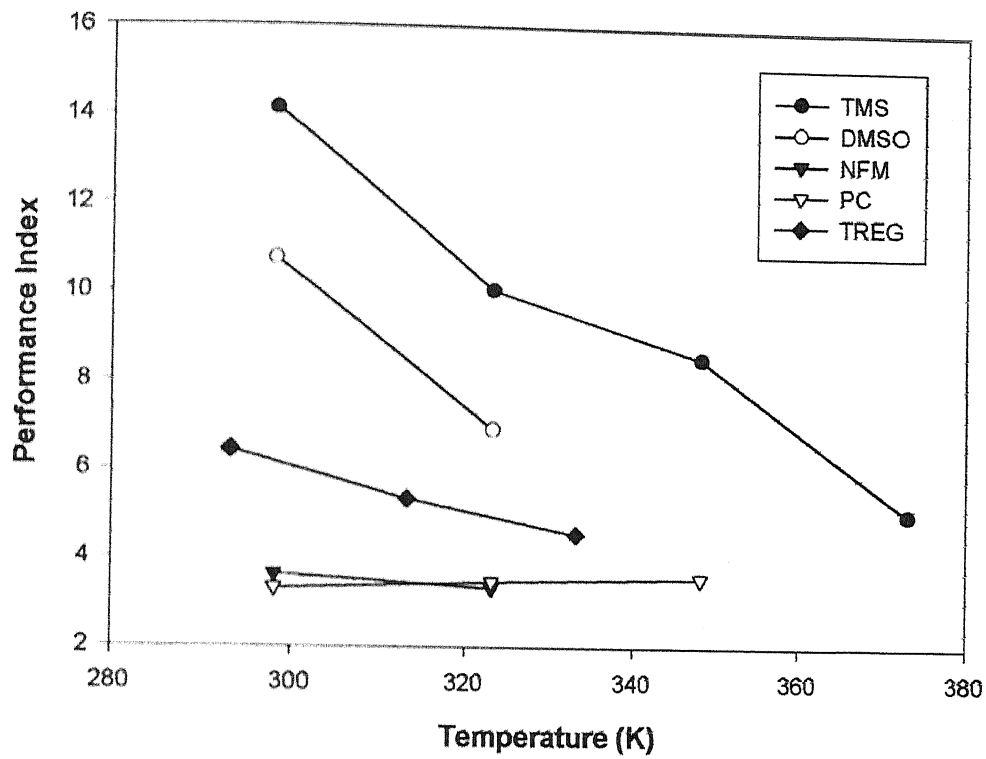


Fig: 6.8 Variation of Performance Index with Temperature

## Chapter 7

### Conclusions and Recommendations

#### Conclusions

Methodologies have been established to estimate the binary interaction parameters from ternary liquid – liquid equilibrium data. Inside Variance Estimation method based on maximum likelihood function has been used for parameter estimation. The UNIFAC and UNIQUAC activity coefficient models have been considered. Both this models are capable of reproducing liquid – liquid equilibria fairly well. It has been observed that the different set of initial guess of parameters may lead to different set of parameters. Although the different set of parameters thus obtained for a particular system may predict the liquid – liquid equilibria for that system fairly well, that cannot be used for other systems.

It has been found that the simultaneous estimation of parameters improves on the above problem. In the parameter estimation technique used in this thesis, the parameters for common pair in different systems are estimated simultaneously. In this way the parameters obtained are found to be generally applicable and not specific to the ternary system from where that have been regressed. The generality of parameters thus obtained has been tested for multicomponent systems. It has been shown that the parameters obtained simultaneously from different ternary systems can be used for prediction of multicomponent liquid – liquid equilibria.

The UNIQUAC parameters estimated are found to be temperature dependent. The temperature dependency of parameters for the systems studied, have been considered. It has been observed that the temperature dependency behaviour of parameters is monotonic with linear relationship for most of the cases. But for the some pairs the temperature dependence does not follow the linear relation.

Binary interaction parameters for the UNIQUAC and UNIFAC model from ternary liquid – liquid equilibrium data have been estimated. Both these models can represent LLE fairly well for aromatic extraction systems. UNIFAC is found to be more suitable for multicomponent LLE.

The extraction abilities of solvents used industrially and the solvents suggested by Molecular Design of Solvents have been estimated. The solvents have been categorized on the basis of a performance index, which incorporates both selectivity and solvent power.

## **Recommendations**

An attempt should be made to discern the physical meaning of interaction parameters. Because these parameters are directly related with interaction energies between components or groups, this relationship along with experimental information can be used to get the binary parameters, which are not specific to ternary system used for their estimation.

More systems should be incorporated into the simultaneous estimation technique, rather than to use only two or three systems. This may lead to more appropriate set of parameters, which can be used for multicomponent systems confidently.

To incorporate temperature dependence in the parameters more proper initial guess can be obtained by extrapolating the parameter values obtained at other temperatures.

UNIFAC parameters for many groups are not yet available for many groups. To use the molecular design of solvents technique efficiently, these parameters must be estimated.

Water if present in small amount with solvents, is known to enhance the selectivity and to broaden the two phase region. Therefore effect of water on the performance of solvents must be considered. For a better performance, water can be mixed with solvents like NMP, which have a good capacity but poor selectivity for aromatics.

## References

- Abrams, D.S. & Prausnitz J.M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.*, 21(1):116-128, 1975.
- Anderson, T. F., Abrams D. S. and Grens E. A. Evaluation of Parameters for Nonlinear Thermodynamic Models. *AIChE J.*, 24(1):20-29, 1978.
- Anderson, T.F. and Prausnitz J.M. Application of the UNIQUAC Equation to Calculation of Multicomponent Phase Equilibria. 2. Liquid-Liquid Equilibria. *Ind. Eng. Chem. Process Des. Dev.*, 17(4):561-567, 1978.
- Bailes, P. J., Hanson C. and Hughes M.A. "Liquid-Liquid Extraction: Nonmetallic materials" *Chem. Eng., Jan.*, 19:115-120, 1976
- Brignole, E. A., S. Bottini and R. Gani "A Strategy for the Design and Selection of Solvents for Separation Processes". *Fluid Phase Equilibria* 29:125-132, 1986.
- Cassell, G. W., M. M. Hassan, and A L. Hines. Liquid-Liquid Equilibria for the Hexane-Benzene-Dimethyl Sulfoxide Ternary System. *J. Chem. Eng. Data*, 34:328-331, 1989.
- Cassell, G. W., N. Dural, and A. L. Hines "Liquid-Liquid Equilibrium of Silfolane-Benzene-Pentane and Sulfolane-Toluene-Pentane". *Ind. Eng. Chem. Res.*, 28:1369-1374, 1989.
- Chen, J., L. Duan, J. Mi, W. Fei, Z. Li "Liquid-Liquid Equilibria of Multi-Component Systems Including n-Hexane, n-Octane, Benzene, Toluene, Xylene and Sulfolane at 298.15 K and Atmospheric Pressure". *Fluid Phase Equilibria*, 173:109-119, 2000
- Chen, J., Z. Li, and L. Duan "Liquid-Liquid Equilibria of Ternary and Quaternary Systems Including Cyclohexane, 1-Heptene, Benzene, Toluene, and Sulfolane at 298.15 K". *J. Chem. Eng. Data*, 45:689-692, 2000
- Choffe, B., C. Raimbault and F. P. Navarre "Extract Aromatics With DMSO". *Hydrocarbon Processing*, 45(5):188-192, 1966.
- Cincotti, A., M. Murru, G. Cao, B. Marongiu, F.Masia, and M. Sannia. "Liquid-Liquid Equilibria of Hydrocarbons with N-Formylmorpholine". *J. Chem. Eng. Data*, 44:480-483, 1999
- Cinelli, E., S. Noc and G. Paret "Extract aromatics with FM" *Hydrocarbon Processing*, 141-144, April 1972.

- Constantinou, L., K. Bagherpour, R. Gani, J. A. Klein and D. T. Wu "Computer Aided Product Design; Problem Formulations, Methodology and Applications" *Comp. Chem. Engng.* 20(6/7):685 – 703, 1996.
- Deal, C. H. and E. L. Derr "Selectivity and Solvency in Aromatic Recovery" *Ind. Eng. Chem. Proc. Des. Dev.*, 3:394-399, 1964
- Esposito, W. R. and C. A. Floudas "Global Optimization of Parameter Estimation of Nonlinear Algebraic Models via the Error-in-Variables Approach". *Ind. Eng. Chem. Res.*, 37:1841-1858, 1998
- Ferreira, P. O., J. B. Ferreira and A. G. Medina "Liquid-Liquid Equilibria for the System N-Methylpyrrolidone + Toluene + n-Heptane: UNIFAC Interaction Parameters for N-Methylpyrrolidone". *Fluid Phase Equilibria*, 16:369-379, 1984.
- Fredenslund, A., R. L. Jones, J. M. Prausnitz "Group Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures". *AIChE J*, 21(6):1086 – 1099, 1975.
- Gani, R., B. Nielsen, and A. Fredenslund "A Group Contribution Approach to Computer Aided Molecular Design". *AIChE J*, 37(9):1318 – 1332, 1991.
- Gani, R., and E. A. Brignole "Molecular design of Solvents for Liquid Extraction based on UNIFAC". *Fluid Phase Equilibria*, 13:331-340, 1983
- Gmehling, J., J. Menke, M. Schiller "Infinite Dilution Activity Coefficients, C1 – C9". *DECHEMA Chemistry data Series*, vol. IX, part 3, 1986.
- Gomis, V., F. Ruiz, J. C. Asensi, M. D. Saquete "Procedure for Checking and fitting experimental liquid – liquid equilibrium data". *Fluid Phase Equilibria*, 129:15 – 19, 1997.
- Gruber, D., M. Topphoff and J. Gmehling. "Measurement of Activity Coefficients at Infinite Dilution Using Gas-Liquid Chromatography. 9. Results for Various Solutes with the Stationary Phases 2-Pyrrolidone and N-Methylformamide" *J. Chem. Eng. Data*, 43:935-940, 1998.
- Lo, Teh C., M. H. I. Baird "Extraction Liquid – Liquid". *Encyclopedia of Separation Technology* vol – 1.
- Macedo, E. A., P. Rasmussen "Liquid – Liquid Equilibrium Data Collection, Supplement 1". *DECHEMA Chemistry Data Series*, vol. V, part 4, 1987.
- Magnussen, T., P. Rasmussen and A. Fredenslund. "UNIFAC Parameter Table for Prediction of Liquid-Liquid Equilibria". *Ind. Eng. Chem. Process Des. Dev.*, 20:331-339, 1981.
- Meniai, A. H. and D. M. T. Newsham "The Selection of Solvents for Liquid – Liquid Extraction". *Trans. IChemE*, 70:78 – 87, 1992.

- Meniai, A. H. and D. M. T. Newsham "Computer – Aided Method for Interaction Parameter Calculations" *Trans. IChemE*, 73:842-848, 1995.
- Meniai, A. H. and D. M. T. Newsham "Molecular solvent design for liquid – liquid extraction using the UNIQUAC model". *Fluid Phase Equilibria*, 158:160, 327 – 335, 1999.
- Mollmann C. and J. Gmehling. "Measurement of Activity Coefficients at Infinite Dilution Using Gas-Liquid Chromatography. 5. Results for N-methylacetamide, N,N-dimethylacetamide, N,N-dibutylformamide, and Sulfolane as Stationary Phases". *J. Chem. Eng. Data*, 42:35-40, 1997.
- Mukhopadhyay, M. "A Thermodynamic Method Based upon the Theory of Regular Solution of Solvents and Process Conditions for Aromatic Extraction" *J. Chem. Tech. Biotechnol.*, 29:634-641, 1979.
- Mukhopadhyay, M, K. R. Dongaonkar "Prediction of Liquid – Liquid Equilibria in Multicomponent Aromatics Extraction Systems by Use of the UNIFAC Group Contribution Model". *Ind. Eng. Chem. Process Des. Dev.* 22:521 – 532, 1983.
- Nelder, J. A., and R. Mead "A Simplex Method for Function Minimization". *Computer Journal*, 7:308 – 313, 1964.
- Prausnitz, J. M., T. Anderson, E. Grens, C. Eckert, R. Hsieh and J. O'Connell "Computer Calculations for Multicomponent Vapor – Liquid and Liquid – Liquid Equilibria". *Prentice – Hall International Series*, 1980.
- Prausnitz, J. M., R. N. Lechenthaler, E. G. Azevedo "Molecular Thermodynamics of Fluid – Phase Equilibria". *Prentice Hall Inc.*, 1986.
- Pretel, E. J., P. A. Lopez, S. B. Bottini, and E. A. Brignole "Computer – Aided Molecular Design of Solvents for Separation Processes". *AIChE J*, 40(8):1349 – 1360, 1994.
- Rawat, B. S., I.B. Gulati and K. L. Mallik "Study of Some Sulfur-group Solvents for Aromatics Extraction by Gas Chromatography". *J. Appl. Chem. Biotechnol*, 26:247-252, 1976.
- Reid, Robert C., J. M. Prausnitz and B. E. Poling "The Properties of Gases and Liquids" *McGraw – Hill International Editions* , 1988.
- Renon H., and J. M. Prausnitz "Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures". *AIChE J.*, 14(1):135 – 144, 1968.
- Salem, A. B. S. H. "Liquid – Liquid Equilibria for the Systems Triethylene Glycol – Toluene – Heptane, Propylene Carbonate – Toluene – Heptane and Carbonate – o-Xylene – Heptane". *Fluid Phase Equilibria*, 86:351 – 361, 1993.

- Salem, A. B. S. H., E. Z. Hamad. "Liquid-Liquid Equilibria of the five component system of n-hexane-n-heptane-toluene-o-xylene-propylene carbonate". *Fluid Phase Equilibria*, 108:231-241, 1995.
- Salem, A. B. S. H., E. Z. Hamad, and M. A. Al-Naafa "Quaternary Liquid-Liquid Equilibria of n-Heptane – Toluene - o-Xylene – Propylene Carbonate". *Ind. Eng. Chem. Res.*, 33:689-692, 1994.
- Sorensen, J. M., and W. Arlt "Liquid – Liquid Equilibrium Data Collection, Binary Data". DECHEMA, *Chemistry Data Series*, vol.V, part .1, 1980.
- Sorensen, J. M., and W. Arlt "Liquid – Liquid Equilibrium Data Collection, Ternary Data". DECHEMA, *Chemistry Data Series*, vol.V, part. 2 1980.
- Sorensen, J. M., and W. Arlt "Liquid – Liquid Equilibrium Data Collection, Ternary and Quaternary". DECHEMA, *Chemistry Data Series*, vol.V, part 3 1980.
- Tiegs, D., J. Gmehling, A. Menke, M. Soares, J. Bastos, P. Alessi and I. Kikic "Infinite Dilution Activity Coefficients, C1 – C9". DECHEMA, *Chemistry Data Series*, vol. IX, part 1, 1986.
- Tiegs, D., J. Gmehling, A. Menke, M. Soares, J. Bastos, P. Alessi and I. Kikic "Infinite Dilution Activity Coefficients, C10 – C36". DECHEMA, *Chemistry Data Series*, vol. IX, part 3, 1994.
- Topphoff M., D. Gruber and J. Gmehling "Measurement of Activity Coefficients at Infinite Dilution Using Gas-Liquid Chromatography. 10. Results for Various Solutes with the stationary Phases Dimethyl Sulfoxide, Propylene Carbonate and N-Ethylformamide" *J. Chem. Eng. Data*, 44:1355-1359, 1999.
- Varhegyi, G. and C. H. Eon "Calculation of the Free Energy Equation Parameters from Ternary Liquid-Liquid Equilibrium Data" *Ind. Eng. Chem. Fundam.*, 16(2), 182-185, 1977.
- Vasquez, V. R., W. B. Whitting. "Regression of binary interaction parameters for thermodynamic models using an inside-variance-estimation method (IVEM)". *Fluid Phase Equilibria.*, 170:235-253, 2000.
- Walas, M. S. "Phase Equilibria in Chemical Engineering". *Butterworth Publishers*, 1985.
- Weidlich, U., H. Rohm, and J. Gmehling. "Measurement of  $\gamma^\infty$  Using GLC. 2. Results for the Stationary Phases N-Formylmorpholine and N-Methylpyrrolidone". *J. Chem. Eng. Data*, 32:450-453, 1987.
- Weimer, R. F. and J. M. Prausnitz "Screen Extraction Solvents This Way" *Hydrocarbon Processing*, 44(9): 237-242, 1965.

Xin, Y., V. R. Vasquez, W. B. Whitting. "Effect of Regression approach in the estimation of nonlinear model parameters on process design and simulation: applications to kinetic and thermodynamic models". *Comp. Chem. Eng.*, 24:1269-1274, 2000

Yorulmaz, Y., F. Karpuzcu "Sulpholane versus Diethylene Glycol in Recovery of Aromatics". *Chem. Eng. Res. Des.*, 63:185 – 190, 1985.

*Hydrocarbon Processing*, 194(sept. 1982)

*Hydrocarbon Processing*, 248(sept. 1970)

*Hydrocarbon Processing*, 195(sept. 1982)

### Bibliography

Note: Other Relevant Literature, not cited in Thesis.

Al-Qattan, M. A. and T. A. Al-Sahhaf. "Liquid-Liquid Equilibria in some Binary and Ternary Mixtures with Tetraethylene Glycol." *J. Chem. Eng. Data* 39:111-113, 1994.

Al-Qattan, M. A. and T. A. Al-Sahhaf. "Liquid-Liquid Equilibria in some Binary and Ternary Mixtures with Tetraethylene Glycol". *J. Chem. Eng. Data* 40:88-90, 1995.

Al – Zayied T. A., T. A. Al – Sahhaf and M. A. Fahim "Measurement o Phase Equilibrium in Multicomponent Systems of Aromatics with N-Methylpyrrolidone and Predictions with UNIFAC". *Fluid Phase Equilibria* , 61:131-144, 1990.

Annesini, M.C., F. Girini and L. Marrelli "Liquid-Liquid Equilibria for Ternary Systems Containing Hydrocarbons and Propylene Carbonate". *J. Chem. Eng. Data*, 30:195-196, 1985.

Antosik, M. and S. Malanowski "Liquid-Liquid equilibria in hydrocarbon + 3-methoxy-propionitrile systems, correlation and prediction". *Fluid Phase Equilibria*, 85:161-170, 1993.

Ashcroft, S. J., A. D. Clayton, and R. B. Shearn. "Liquid-Liquid Equilibria for Three Ternary and Six Quaternary Systems Containing Sulfolane, n-Heptane, Toluene, 2-Propanol, and Water at 303.15 K". *J. Chem. Eng. Data*, 27:148:151, 1982

Bottini, S. B. "Liquid-Liquid Equilibria for the System Toluene-Isooctane-Diethylene Glycol Methyl Ether". *J. Chem. Eng. Data*, 31:84-86, 1986.

Cassell, G. W., M. M. Hassan, and A. L. Hines "Correlation of the Phase Equilibrium Data for the Heptane-Toluene-Sulfolane and Heptane-Xylene-Sulfolane Systems". *J. Chem. Eng. Data*, 34:434-438, 1989.

De Fre, R. M., and L. A. Verhoeve "Phase Equilibria in Systems composed of an Aliphatic and an Aromatic Hydrocarbon and Sulfolane". *J. Appl. Chem. Biotechnol.* 26:469-487, 1976.

- Francis, A. W. "Solvent Selectivity for Hydrocarbons Measured by Critical Solution Temperature". *Ind. Eng. Chem. Res.*, 36(8):664 – 771, 1944.
- Ferreira, P. O., J. C. Bastos, and A. G. Medina. "Infinite Dilution Activity Coefficients for Aromatic and Nonaromatic Compounds in N-Methylpyrrolidone, Ethylene Glycol, and Mixtures of the Two Solvents". *J. Chem. Eng. Data*, 32:25-31, 1987.
- Hassan, M. S., and M. A. Fahim "Corelation of Phase Equilibria of Naphtha Reformate with Sulfolane". *J. Chem. Eng. Data*, 33:162-165, 1988.
- Hughes, M. A., and Y. Haoran. "Liquid-Liquid Equilibria for Separation of Toluene from Heptane by Benzyl Alcohol Tri(ethylene glycol) Mixtures". *J. Chem. Eng. Data*, 35:467-471, 1990.
- Krummen, M., D. Gruber and J. Gmehling "Measurement of Activity Coefficients at Infinite Dilution in Solvent Mixtures Using the Dilutor Technique" *Ind. Eng. Chem. Res.*, 39:2114-2123, 2000
- Lee S. and H. Kim "Liquid-Liquid Equilibria for Ternary Sytems Sulfolane + Octane + Benzene, Sulfolane + Octane + Toluene, Sulfolane + Octane + p-Xylene". *J. Chem. Eng. Data*, 40:499-503, 1995
- Lee S. and H. Kim "Liquid-Liquid Equilibria for Ternary Sytems Sulfolane + Octane + Benzene, Sulfolane + Octane + Toluene, and Sulfolane + Octane + p-Xylene at Elevated Temperatures". *J. Chem. Eng. Data*, 43:358-361, 1998
- Letcher, T. M., G. G. Redhi, S. E. Radloff. "Liquid-Liquid Equilibria of the Ternary Mixtures with Sulfolane at 303.15 K". *J. Chem. Eng. Data*, 41:634-638, 1996
- Letcher, T. M. and P. K. Naicker "Liquid-Liquid Equilibria for Mixtures of an Alkane + Aromatic Hydrocarbon + 1,4- Dicyanobutane at 298.15 K" *J. Chem. Eng. Data*, 45:104-109, 2000
- Mondragon G., M., A. R. Martinez and A. Trejo "Liquid-Liquid equilibria for ternary systems. I. C<sub>6</sub>-isomers + sulfolane + toluene at 298.15 K". *Fluid Phase Equilibria*, 64:291-303, 1991.
- Mukhopadhyay, M. and A. S. Pathak. "Infinite-Dilution Activity Coefficients from Ebulliometric Isobaric Bubble Point-Composition Data of Hydrocarbon-Sulfolane Systems". *J. Chem. Eng. Data*, 31:148-152, 1986
- Mukhopadhyay, M. and A. S. Pathak. "LLE Data for Aromatics Calculations Using a Modified UNIFAC Model". *Ind. Eng. Chem. Process Des. Dev.*, 25:733-736, 1986
- Mukhopadhyay, M. and K. Shasranaman "Computation of Multicomponent Liquid-Liquid Equilibrium Data for Aromatics Extraction Systems". *Ind. Eng. Chem. Process Des. Dev.*, 21:632-640, 1982

Nagata, I., and S. Nakamura. "Liquid-Liquid equilibria of (cyclohexane + acetonitrile + methylcyclohexane + toluene) and of {(acetonitrile + methylcyclohexane) + benzene or + toluene or + cyclohexane or + chlorobenzene} at 298.15 K". *J. Chem. Thermodynamics*, 17:1103-1110, 1985

Nagpal, J. M. and B. S. Rawat. "Liquid-Liquid Equilibria for Toluene-Heptane-N-Methyl Pyrrolidone and Benzene-Heptane Solvents". *J. Chem. Tech. Biotech.*, 31:146-150 1981

Naithani, J., M. K. Khanna, S. M. Nanoti, and B. S. Rawat. "Quaternary Liquid-Liquid Equilibrium Studies on Hydrocarbon-Solvent Systems". *J. Chem. Eng. Data*, 37:104-106, 1992.

Odele, O., and S. Macchietto "Computer Aided Molecular Design A Novel Method for Optimum Solvent Selection". *Fluid Phase Equilibria*, 82:47 – 54, 1993.

Radwan, G. M., S. A. Al-Muhtaseb, and M. A. Fahim "Liquid – Liquid Equilibria for the Extraction by Dimethylformamide / Ethylene Glycol mixed Solvent". *Fluid Phase Equilibria* , 129:175 – 186, 1997.

Rahman, M., P. Mikitenko, L. Asselineau "Solvent Extraction of Aromatics from Middle Distillates". *Chemical Eng. Sci.*, 39(11):1543 – 1558, 1984.

Rawat, B. S. and I. B. Gulati "Liquid-Liquid Equilibrium Studies for Separation of Aromatics". *J. Appl. Chem. Biotechnol.* 26:425-435, 1976.

Rawat, B. S. and G. Prasad. "Liquid-Liquid Equilibria for Benzene-n-Heptane Systems with Triethylene Glycol, Tetraethylene Glycol, and Sulfolane Containing Water at Elevated Temperatures". *J. Chem. Eng. Data*, 25:227-230, 1980

## Appendix A

### Activity Coefficient Models

#### A.1 UNIQUAC Activity Coefficient Model

The Universal Quasi Chemical (UNIQUAC) model, was developed by (Abrams & Prausnitz, 1975), to express the excess Gibbs free energy of mixtures. This model uses two adjustable parameters per binary. The UNIQUAC equation contains two parts, a combinatorial part and a residual part. The combinatorial part takes into account the composition, size and shape of the constituent molecules and contains pure component properties only. The residual part takes into account the intermolecular forces and contains two adjustable parameters. The molar excess Gibbs energy for a mixture is given by the sum of

$$\frac{g^E(\text{combinatorial})}{RT} = \sum_{i=1}^n x_i \ln \frac{\Phi_i}{x_i} + \frac{z}{2} \sum_{i=1}^n q_i x_i \ln \frac{\theta_i}{\Phi_i} \quad (\text{A.1})$$

and

$$\frac{g^E(\text{residual})}{RT} = - \sum_{i=1}^n q_i x_i \ln \left( \sum_{j=1}^n \theta_j \tau_{ji} \right) \quad (\text{A.2})$$

where

$$\Phi_i \text{ is segment or volume fraction of component } i = \frac{r_i x_i}{\sum_{i=1}^n r_i x_i};$$

$$\theta_i \text{ is area fraction of component } i = \frac{q_i x_i}{\sum_{i=1}^n q_i x_i};$$

$r_i$  is volume parameter of component  $i$ ;

$q_i$  is surface area parameter of component  $i$ ;

$\tau_{ji}$  is adjustable parameter, given by

$$\tau_{ji} = \exp \left\{ - \frac{(u_{ji} - u_{ij})}{RT} \right\} = \exp \left\{ - \frac{a_{ji}}{T} \right\} \quad (\text{A.3})$$

$u_{ij}$  is the interaction energy for the interaction of molecules of component  $i$  with the molecules of component  $j$  ;

and  $u_{ij} = u_{ji}$

$a_{ij}$  is the interaction parameter between component  $i$  and component  $j$  ;

and  $a_{ij} \neq a_{ji}$

$z$  is the coordination number, which is usually taken as 10.

From equations (AII.1) and (AII.2) the activity coefficient for any component  $i$ , is given by

$$\ln \gamma_i = \ln \gamma_i^c (\text{combinatorial}) + \ln \gamma_i^R (\text{residual}) \quad (\text{A.4})$$

where

$$\ln \gamma_i^c = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_{j=1}^n x_j l_j \quad (\text{A.5})$$

and

$$\ln \gamma_i^R = q_i \left[ 1 - \ln \left( \sum_{j=1}^n \theta_j \tau_{ji} \right) - \sum_{j=1}^n \frac{\theta_j \tau_{ij}}{\left( \sum_{k=1}^n \theta_k \tau_{kj} \right)} \right] \quad (\text{A.6})$$

and

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \quad (\text{A.7})$$

The pure component parameters are, respectively, measures of molecular van der Waals volumes and molecular surface areas. They are calculated as the sum of the group volume and group area parameters,  $R_k$  and  $Q_k$

$$r_i = \sum_k v_k^{(i)} R_k; \quad q_i = \sum_k v_k^{(i)} Q_k \quad (\text{A.8})$$

where  $v_k^{(i)}$ , always an interger, is the number of groups of type  $k$  in molecule  $i$ . Group parameters  $R_k$  and  $Q_k$  are normally obtained from van der Waals group volumes and surface areas as shown.

## A.2 UNIFAC Activity Coefficient Model

This group contribution method combines the solution of functional groups concept with a model for activity coefficients based on an extension of the quasi chemical theory of liquid mixtures, hence known as UNIFAC (UNIQUE Functional-group Activity Coefficients). This model contains two adjustable parameters per pair of functional groups. The fundamental idea of a solution-of-groups model is to utilize existing phase equilibrium data for predicting phase equilibria of systems for which no experimental data are available. Like the UNQUAC method, in this method also the activity coefficient of a component in a mixture is represented as product of a combinatorial and a residual activity coefficient. Hence the activity coefficient is given by

$$\ln \gamma_i = \ln \gamma_i^c(\text{combinatorial}) + \ln \gamma_i^R(\text{residual}) \quad (\text{A.4})$$

The combinatorial term is same as used for UNIFAC and given by (A.5). Only pure component parameters are needed for this part. Parameters  $r_i$  and  $q_i$  are calculated from group parameters,  $R_k$  and  $Q_k$ . These group parameters are obtained from the van der Waals group volume and surface areas  $V_k$  and  $A_k$  as given by (Reid et. al., 1988)

$$R_k = \frac{V_k}{15.17} \quad \text{and} \quad Q_k = \frac{A_k}{2.5 \times 10^9}$$

The residual part, which is different from UNQUAC and involves the interactions between groups, is given by

$$\ln \gamma_i^R = \sum_k v_k^{(i)} \left[ \ln \Gamma_k - \ln \Gamma_k^{(i)} \right] \quad (\text{A.9})$$

$\Gamma_k$  is the group residual activity coefficient and  $\Gamma_k^{(i)}$  is the residual activity coefficient of group  $k$  in a reference solution containing only molecules of type  $i$ . The  $v_k^{(i)}$  is the number of groups of type  $k$  in the molecule  $i$ .

The group activity coefficient  $\Gamma_k$  is given by

$$\ln \Gamma_k = Q_k \left[ 1 - \ln \left( \sum_m \Theta_m \Psi_{mk} \right) - \sum_m \left( \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}} \right) \right] \quad (\text{A.10})$$

Above equation (A.10) also hold for  $\ln \Gamma_k^{(i)}$ . In this equation  $\Theta_m$  is the area fraction of group  $m$ , and the sums are over all different groups.  $\Theta_m$  is given by

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad (\text{A.11})$$

Where  $X_m$  is the mole fraction of group in the mixture. The group interaction parameter  $\Psi_{mn}$  is given by

$$\Psi_{mn} = \exp \left\{ - \left[ \frac{U_{mn} - U_{mm}}{RT} \right] \right\} \equiv \exp \left\{ - \frac{a_{mn}}{T} \right\} \quad (\text{A.12})$$

Where  $U_{mn}$  is a measure of the energy of interaction between group's  $m$  and  $n$ . The group interaction parameters must be evaluated from experimental phase equilibrium data.

## Appendix B

### Simplex method for function minimization

Nelder J. A. and R. Mead (Nelder and Mead, 1964) have described the simplex method for minimization of a function of  $n$  variables. Which depends on the comparison of function values at the  $(n+1)$  vertices of a general simplex, followed by the replacement of the vertex with the highest value by another point.

Consider the minimization of a function of  $n$  variables, without constraints.  $P_0, P_1, \dots, P_n$  are the  $(n+1)$  points in  $n$  dimensional space defining the current “simplex”. Let the function value at  $P_i$  is given by  $y_i$ , and define

$$y_h = \max_i(y_i) \text{ where suffix } h \text{ is for “high”}$$

and

$$y_l = \min_i(y_i) \text{ where suffix } l \text{ is for “low”}$$

Let the point  $\bar{P}$  is the centroid of the points with  $i \neq j$ , and  $[P_i P_j]$  is the distance between  $P_i$  and  $P_j$ . At each stage in the process  $P_h$  is replaced by a new point; three operations are used – *reflection*, *contraction*, and *expansion*. These operations are defined as follows:

The *reflection* of point  $P_h$  is denoted by  $P^*$ , and its coordinated are defined by the relation

**Reflection:** 
$$P^* = (1 + \alpha)\bar{P} - \alpha P_h$$

Where  $\alpha$  is a positive constant known as *reflection coefficient*. Thus the  $P^*$  is on the line joining the points  $P_h$  and  $\bar{P}$ , on the far side of  $\bar{P}$  from  $P_h$  with  $[P^* \bar{P}] = \alpha[P_h \bar{P}]$ . If the function value at the reflection point that is  $y^*$ , lies between  $y_h$  and  $y_l$ , then  $P_h$  is replaced by  $P^*$  and we start again with a new simplex.

If  $y^* < y_l$ , i.e. if reflection has produced a new minimum, then we expand  $P^*$  to  $P^{**}$  by the relation

**Expansion:** 
$$P^{**} = \gamma P^* + (1 - \gamma)\bar{P}.$$

The *expansion coefficient*  $\gamma$ , which is greater than unity, is the ratio of the distance  $[P^{**} \bar{P}]$  to  $[P^* \bar{P}]$ .

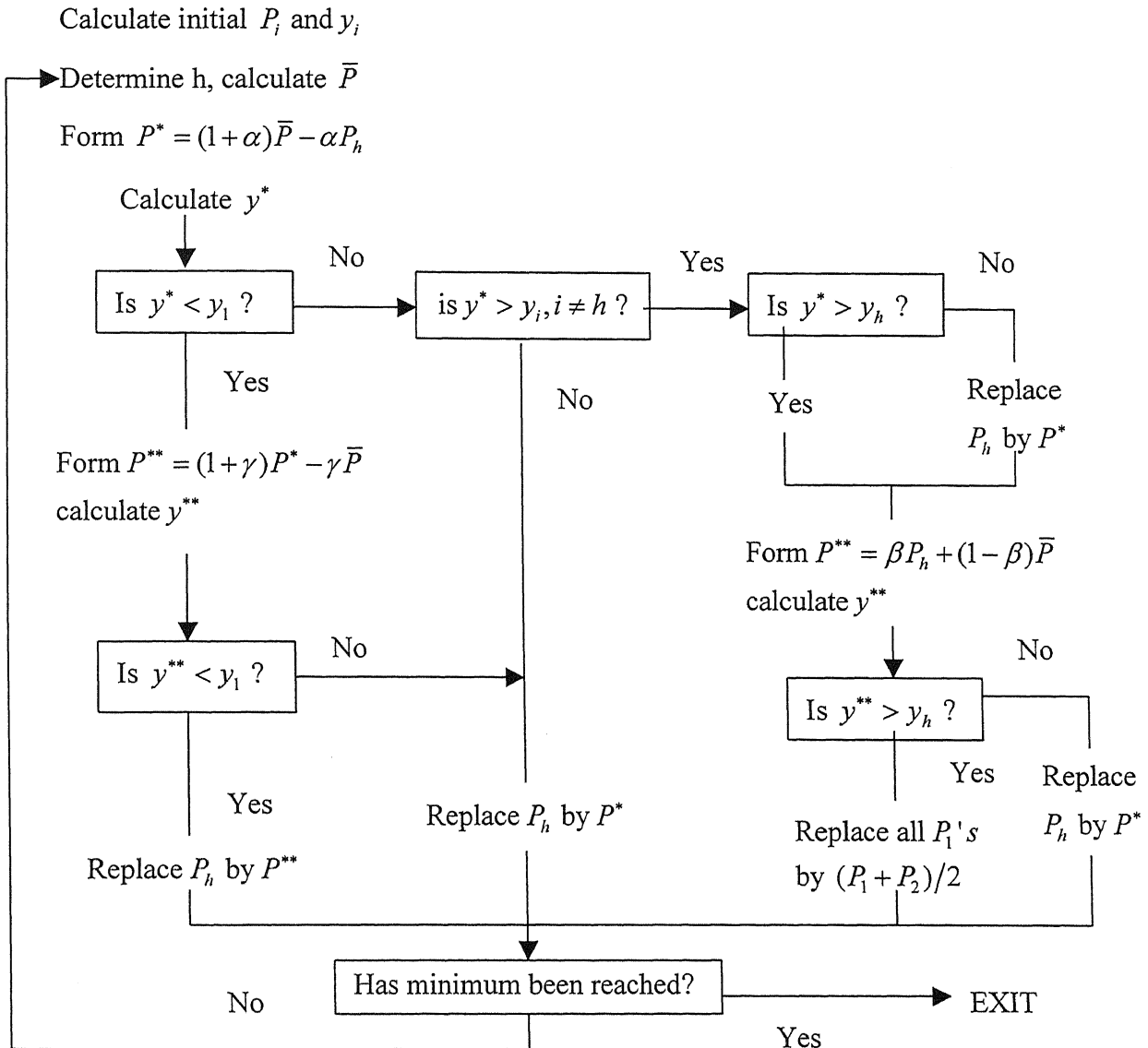
If  $y^{**} < y_l$ , we replace  $P_h$  by  $P^{**}$  and restart the whole process; but if  $y^{**} > y_l$  then we have a failed *expansion*, and we replace  $P_h$  by  $P^*$  before restarting.

If on reflecting  $P$  to  $P^*$  we find that  $y^* > y^*$  for all  $i \neq h$ , i.e., replacing  $P$  by  $P^*$  leaves  $y^*$  the maximum, then we define a new  $P_h$  to be either the old  $P_h$  or  $P^*$ , whichever has the lower  $y$  value, and form

**Contraction:** 
$$P^{**} = \beta P_h + (1 - \beta) \bar{P}$$

The contraction coefficient  $\beta$  lies between 0 and 1 and is the ratio of the distance  $[P^{**} \bar{P}]$  to  $[P \bar{P}]$ . We then accept  $P^{**}$  for  $P_h$  and restart, unless  $y^{**} > \min(y_h, y^*)$ , i.e. the contracted point is worse than the better of  $P_h$  and  $P^*$ . For such a failed contraction we replace all the  $P_i$ 's by  $(P_i + P_l)/2$  and restart the process.

### Flow chart



## Appendix C

### MATLAB Computer Programs

#### A.1 Program for initial guess using activity difference approach

```

%*****
% FILE: initial_guess.m
%*****
% INCLUDE FILE: activity_objective.m
% INCLUDE FILE: uniquac.m
% INCLUDE FILE: exp_tie.txt
% INCLUDE FILE: out.txt
% SPECIFY temperature in this FILE
% SPECIFY number of tie lines in FILE "activity_objective"
% SPECIFY Rk Qk in FILE "activity_objective"
%*****
global exp_tie;
global temp;
global no_component;
global m;
temp = 298.15; % temperature
% OPEN FILE "exp_tie.txt"
fid =fopen('exp_tie.txt');
% READ tie line data in a MATRIX of (6,m)
exp_tie = fscanf(fid,'%g %g',[6 inf]);
% CLOSE the FILE "exp_tie.txt"
fclose(fid);
exp_tie = exp_tie'; % TRANSPOSE the MATRIX to (m,6)
% INITIAL guess of parameters
% ANY anitial guess will work
a_inter0 = [263.884 798.177 -165.976 -49.8531 54.0035 176.911]
;
% Number of function evaluation
options(14)=5000;
% CALL FILE "activity_objective" for objective function
% CALL "leastsq" for least square minimization
a_inter = leastsq('activity_objective',a_inter0,options)
% OPEN FILE "out.txt"
fiid = fopen('out.txt','a'); % PRINT temperature
fprintf(fiid,'temprature = %g \n',temp);
% PRINT initial guess
fprintf(fiid,'initial guess = %g %g %g %g %g %g\n',a_inter0);
% PRINT parameters
fprintf(fiid,'parameters_act = %g %g %g %g %g %g\n',a_inter);
% CLOSE the FILE "out.txt"
fclose(fiid);

```

```

% *****
% FILE: uniquac.m
% *****
function gammal = gamma(no_component ,x,
temp,Rk,Qk,a_interaction)
% CALCULATE zi(i,j)
for i = 1:no_component
    for j = 1:no_component
        z_i(i,j)=exp(-(a_interaction(i,j)/temp));
    end
end
sum_1 = 0;
sum_2 = 0;
% SUMMATION x(i)*R(i)
% SUMMATION x(i)*Q(i)
for i = 1: no_component
    theta_zi(i) = 0;
    sum(i) = 0;
    sum_1=sum_1+x(i)*Rk(i);
    sum_2=sum_2+x(i)*Qk(i);
end
sum_x_l = 0;
for i= 1:no_component
    phi(i)=(x(i)*Rk(i))/sum_1;
    theta(i)=(x(i)*Qk(i))/sum_2;
    l(i)=5*(Rk(i)-Qk(i))+1-Rk(i);
    sum_x_l=sum_x_l + x(i)*l(i);
end
for i=1:no_component
    for j=1:no_component
        theta_zi(i)=theta_zi(i) + theta(j)*z_i(j,i);
    end
end
% SUMMATION
for i=1:no_component
    for j=1:no_component
        sum(i)=sum(i) + (theta(j)*z_i(i,j))/theta_zi(j);
    end
end
% ESTIMATE gamma vector
for i=1:no_component
    ln_gamma_r(i)= Qk(i)*(1-log(theta_zi(i))-sum(i));
    ln_gamma_c(i)=log(phi(i)/x(i))+5*Qk(i)*(log(theta(i)/phi(i)))+
    l(i)-(phi(i)/x(i))*sum_x_l;
    gammal(i)=exp(ln_gamma_c(i)+ln_gamma_r(i));
end

```

```

%*****
% FILE unifac.m
%*****
function gammal = unifac(no_component ,no_group,v,x,
temp,Rk,Qk,a)
% INITIATE
sum1 = 0;
sum2 = 0;
sum3 = 0;
sum4 = 0;
sum6 = 0;
% no_compoent = Number of components
% no_group     = Total number of groups
for i=1:no_component
    for k=1:no_group
        sum77(i,k)=0;
        sum88(i,k)=0;
    end
end
for i=1:no_component
    r(i) = 0;
    q(i) = 0;
    sum11(i)=0;
    sum66(i)=0;
    sum9(i)=0;
    sum10(i)=0;
end
for j=1:no_group
    sum5(j)=0;
    sum7(j)=0;
    sum8(j)=0;
end
for i=1:no_component
    for j=1:no_group
        r(i) = r(i)+v(i,j)*Rk(j);
        q(i) = q(i) +v(i,j)*Qk(j);
        sum4 = sum4+v(i,j)*x(i);
    end
end
for i=1:no_component
    sum1 = sum1+r(i)*x(i);
    sum2 = sum2+q(i)*x(i);
    l(i) = 5*(r(i)-q(i))-(r(i)-1);
    sum3 = sum3+x(i)*l(i);
end
for i=1:no_component

```

```

        ln_gamma_c(i) =
log(r(i)/sum1)+5*q(i)*log((q(i)*sum1)/(r(i)*sum2))...
                                +1(i)-(r(i)*sum3)/sum1;
end
for j=1:no_group
    for i=1:no_component
        sum5(j)=sum5(j)+v(i,j)*x(i);
    end
end
for j=1:no_group
    X(j)=sum5(j)/sum4;
    sum6 = sum6+Qk(j)*X(j);
end
for j=1:no_group
    xi(j)=(Qk(j)*X(j))/sum6;
end
for k=1:no_group
    for j=1:no_group
        zi(j,k)=exp(-a(j,k)/temp);
        sum7(k)=sum7(k)+xi(j)*zi(j,k);
    end
end
for k=1:no_group
    for j=1:no_group
        sum8(k) = sum8(k)+(xi(j)*zi(k,j))/sum7(j);
    end
end
for k=1:no_group
    ln_gamma_k(k) = Qk(k)*(1-log(sum7(k))-sum8(k));
end
for i=1:no_component
    for j=1:no_group
        sum11(i)=sum11(i)+v(i,j);
    end
end
for i=1:no_component
    for j=1:no_group
        XX(i,j)=v(i,j)/sum11(i);
        sum66(i)=sum66(i)+Qk(j)*XX(i,j);
    end
end
for i=1:no_component
    for j=1:no_group
        xixi(i,j)=Qk(j)*XX(i,j)/sum66(i);
    end
end
for i=1:no_component

```

```

    for k=1:no_group
        for j=1:no_group
            sum77(i,k)=sum77(i,k)+xixi(i,j)*zi(j,k);
        end
    end
end
for i=1:no_component
    for k=1:no_group
        for j=1:no_group
            sum88(i,k)=sum88(i,k)+(xixi(i,j)*zi(k,j))/sum77(i,j);
        end
    end
end
for i=1:no_component
    for k=1:no_group
        ln_gamma_i_k(i,k)=Qk(k)*(1-log(sum77(i,k))-sum88(i,k));
    end
end
for i=1:no_component
    for j=1:no_group
        sum9(i)=sum9(i)+v(i,j)*ln_gamma_k(j);
        sum10(i)=sum10(i)+v(i,j)*ln_gamma_i_k(i,j);
    end
    ln_gamma_r(i) = sum9(i)-sum10(i);
    gammal(i) = exp(ln_gamma_c(i)+ln_gamma_r(i));
end

```

```

%*****
% FILE: nrt1.m
%*****
function gammal = gamman(no_component ,x, temp,alpha
,a_interaction)
for i = 1:no_component
for j = 1:no_component
    tau(i,j)=a_interaction(i,j)/temp;
    G(i,j)=exp(-alpha*tau(i,j));
end
end
for i=1:no_component
    sum1(i) = 0;
    sum2(i) = 0;
    sum3(i) = 0;
end
for i=1:no_component
    for j=1:no_component
        sum1(i)=sum1(i)+tau(j,i)*G(j,i)*x(j);
        sum2(i)=sum2(i)+G(j,i)*x(j);
    end
end
for i=1:no_component
    for j=1:no_component
        sum3(i)=sum3(i)+((x(j)*G(i,j))/sum2(j))*(tau(i,j)-
sum1(j)/sum2(j));
    end
end
for i=1:no_component
    gammal(i) = exp((sum1(i)/sum2(i))+sum3(i));
end

```

## A.2 Program for estimation of parameters from ternary LLE data for a particular ternary system

```
%*****
% FILE: initial.m
%*****
% INCLUDE FILE: objective.m
% INCLUDE FILE: estimation.m
% INCLUDE FILE: lle_equation.m
% INCLUDE FILE: uniquac.m          % same as for initial guess
% INCLUDE FILE: unifac.m          % same as above
% INCLUDE FILE: nrtl.m            % same as above
% INCLUDE FILE: exp_tiel.txt
% INCLUDE FILE: out.txt
% SPECIFY temperature in "estimation" FILE
% SPECIFY number of tie lines in "objective
% SPECIFY Rk and Qk in estimation FILE

global p1;      % DECLARE global to objective function
global rms;     % DECLARE global to rmsd
global itr;     % DECLARE global to number of ITERATIONS
itr = 0;        % Start ITERATION number
% SET number of function evaluation
options(14) = 5000;
% Initial Guess of Parameters
% Arrange the parameters like
% a_inter0 = [ (1,2) (1,3) (2,1) (2,3) (3,1) (3,2)];
a_inter0 = [-116.105 590.329 157.958 13.5982 78.543 62.2065];
% CALL the "objective" FILE for objective function
% CALL "fmins" for minimization
a_inter = fmins('objective',a_inter0,options)
% OPEN FILE "out.txt" for output
fiid = fopen('out.txt','a');
% PRINT initial guess used
fprintf(fiid,'initial guess = %g %g %g %g %g %g \n',a_inter0);
% PRINT parameters estimated
fprintf(fiid,'parameters = %g %g %g %g %g %g \n',a_inter);
% PRINT objective function
fprintf(fiid,'L = %g \n',p1); % PRINT rmsd values
fprintf(fiid,'p1 = %g \n',rms);
% PRINT iteration numbers
fprintf(fiid,'iterations = %d',itr);
% CLOSE FILE "out.txt"
fclose(fiid);
```

```

%*****
% FILE: objective
%*****
function L = objective(a_inter) % FUNCTION DECLARE
global p1;
global rms;
global itr;
m=10;          % Number of experimental tie lines
% INCREASE Number of iteraton by 1
itr = itr+1
% CONVERT the parameters in MATRIX form
% a_interaction = [ 0      (1,2)      (1,3)
%                  (2,1)  0          (2,3)
%                  (3,1) (3,2)      0  ];
a_interaction = [0 a_inter(1)  a_inter(2);
                 a_inter(3) 0 a_inter(4);
                 a_inter(5) a_inter(6) 0];

%*****
% OPEN FILE "exp_tie.txt" for Experimental data
fid = fopen('exp_tie.txt','r');
% READ tie line data in (6,m) MATRIX
exptiel = fscanf(fid,'%g %g',[6 inf]);
% CLOSE "exp_tiel.txt"
fclose(fid);
% TAKE the transpose of MATRIX to make it (m,6)
exp_tie = exptie';
% INITIATE sum's
sum1=0;sum2=0;sum3=0;sum4=0;
% INITIATE v's
v1=0;v2=0;v3=0;v4=0;
% CALL "estimation" for tie line estimation
% STORE them in a MATRIX
est_tie = estimation(m,exp_tie,a_interaction);
% CALCULATE errors
error = exp_tie - est_tie;
% CALCULATE sum of errors
for i = 1:m
    sum1= sum1+error(i,1);
    sum2= sum2+error(i,2);
    sum3= sum3+error(i,4);
    sum4= sum4+error(i,5);
end
% AVERAGE of errors
sum1 = sum1/m; sum2 = sum2/m; sum3 = sum3/m;
sum4 = sum4/m;
% ESTIMATE variances

```

```

for i = 1:m
    v1 = v1+(error(i,1)-sum1)^2;
    v2 = v2+(error(i,2)-sum2)^2;
    v3 = v3+(error(i,4)-sum3)^2;
    v4 = v4+(error(i,5)-sum4)^2;
end
v1=v1/(m-1);v2=v2/(m-1);v3=v3/(m-1);v4=v4/(m-1);
% INITIATE
tem = 0;
% CALCULATE summation
for i=1:m
    tem = tem + (error(i,1))^2/v1+(error(i,2))^2/v2+...
               (error(i,4))^2/v3+(error(i,5))^2/v4;
end
% CALCULATE the objective function
L = 2*m*log(2*pi)+(m/2)*log(v1*v2*v3*v4)+(1/2)*tem
p1 = L;
sum_square = 0;
% CALCULATE the rmsd
for i=1:m
    for j=1:6
        sum_square = sum_square+(est_tie(i,j)-exp_tie(i,j))^2;
    end
end
rms = 100*(sum_square/(6*m))^0.5
% RETURN
%*****
% FILE: estimation.m
%*****
% FUNCTION DECLARE
function estimate = estimation1(m,exp_tie,a_interaction)
% Rk for three components
Rk = [4.4998 3.19051 4.0356];
% Qk for three components
Qk = [3.856 2.4 3.2 ];
% SPECIFY temperature
temp =298.15;
for i=1:m
% ESTIMATE mid point of tie lines
    z_1 = (exp_tie(i,1)+exp_tie(i,4))/2;
    z_2 = (exp_tie(i,2)+exp_tie(i,5))/2;
% initial guess of a tie line
    X0 = exp_tie(i,:);
% CALL "lle_equation" for setting LLE equations
% CALL "fosolve" for Solving equations

```

```

X =
fsolve('lle_equation',X0,[],[],z_1,z_2,Rk,Qk,a_interaction,temp);
% STORE the tie lines in a MATRIX
    for j=1:6
        est(i,j) = X(j);
    end
    estimate = est;
end

% *****
% FILE: lle_equation.m
% *****
% FUNCTION DECLARE
function equation =
lle_equation(X,z_1,z_2,Rk,Qk,a_interaction,temp)
% number of components
no_component = 3;
% two phase compositions
x(1) = X(1);
x(2) = X(2);
x(3) = X(3);
y(1) = X(4);
y(2) = X(5);
y(3) = X(6);
% CALL "uniquac" for activity coefficients for PHASE I
gamma_I = uniquac(no_component , x ,
temp,Rk,Qk,a_interaction);

% CALL "uniquac" for activity coefficients for PHASE II
gamma_II = uniquac(no_component , y ,
temp,Rk,Qk,a_interaction);
% SET the LLE equations
equation = [
    (z_1-X(1))*(X(5)-X(2))-(X(4)-X(1))*(z_2-X(2));
    X(1)*gamma_I(1) - X(4)*gamma_II(1);
    X(2) * gamma_I(2) - X(5) * gamma_II(2);
    X(3) * gamma_I(3) - X(6) * gamma_II(3);
    X(1) + X(2) + X(3)-1;
    X(4) + X(5) + X(6)-1];
% RETUREN

```

### A.3 Program for Simultaneous estimation of parameters from three ternary systems

```

%*****
% FILE: initial_simult.m
%*****
% INCLUDE FILE: objective_simult.m
% INCLUDE FILE: estimation1.m
% INCLUDE FILE: estimation2.m
% INCLUDE FILE: estimation3.m
% INCLUDE FILE: lle_equation.m           % same as for above
% INCLUDE FILE: uniquac.m               % same as for above
% INCLUDE FILE: unifac.m                 % same as for above
% INCLUDE FILE: nrtl.m                   % same as for above
% INCLUDE FILE: exp_tie1.txt
% INCLUDE FILE: exp_tie2.txt
% INCLUDE FILE: exp_tie3.txt
% INCLUDE FILE: out.txt
% SPECIFY temperature in all "estimation" FILE
% SPECIFY number of tie lines in "objective_simult
% SPECIFY Rk and Qk in each estimation FILE
global p1;      % DECLARE global to objective function 1
global p2;      % DECLARE global to objective function 2
global p3;      % DECLARE global to objective function 3
global rms1;    % DECLARE global to rmsd1
global rms2;    % DECLARE global to rmsd2
global rms3;    % DECLARE global to rmsd3
global itr;     % DECLARE global to number of ITERATIONS
itr = 0;        % Start ITERATION number
% SET number of function evaluation
options(14) = 5000;
% Initial Guess of Parameters,,,,,
% Dont Repeat parameters which are common
% Arrange the parameters like
% a_inter0 = [ (1,2) (1,3) (2,1) (2,3) (3,1) (3,2).... %
For First System
%              (1,2) (2,1) (2,3) (3,2) .... %
For Second System
%              (1,2) (2,1) (2,3) (3,2)]; %
For Third System
% NOTE that parameters (1,3) and (3,1) are common to all
systems
a_inter0 = [-116.105 590.329 157.958 13.5982 78.543 62.2065...
            167.265 -137.203 80.06 37.5965...
            272.432 -212.1113 120.6137 56.2235];
% CALL the "objective_simult" FILE for objective function
% CALL "fmins" for minimization

```

```

a_inter = fmins('objective_simult',a_inter0,options)

% OPEN FILE "out.txt" for output
fiid = fopen('out.txt','a');
% PRINT initial guess used
fprintf(fiid,'initial guess = %g %g %g %g %g %g %g %g %g %g %g %g %g %g %g\n',a_inter0);
% PRINT parameters estimated
fprintf(fiid,'parameters = %g %g %g %g %g %g %g %g %g %g %g %g %g %g %g\n',a_inter);
% PRINT objective functions
fprintf(fiid,'L = %g %g %g\n',p1,p2,p3);
% PRINT rmsd values
fprintf(fiid,'p1 = %g %g %g\n',rms1,rms2,rms3);
% PRINT iteration numbers
fprintf(fiid,'iterations = %d',itr);
% CLOSE FILE "out.txt"
fclose(fiid);

%*****
% FILE: objective_simult
%*****
function L = objective_simult(a_inter) % FUNCTION DECLARE
global p1;
global p2;
global p3;
global rms1;
global rms2;
global rms3;
global itr;
m1=10; % Number of experimental tie lines
m2=10; % Number of experimental tie lines
m3=10; % Number of experimental tie lines
% INCREASE Number of iteraton by 1
itr = itr+1
% CONVERT the parameters in MATRIX form for System 1
% a_interaction = [ 0 (1,2) (1,3)
% (2,1) 0 (2,3)
% (3,1) (3,2) 0 ];
a_interaction1 = [0 a_inter(1) a_inter(2);
a_inter(3) 0 a_inter(4);
a_inter(5) a_inter(6) 0];
% CONVERT the parameters in MATRIX form for System 2
a_interaction2 = [0 a_inter(7) a_inter(2);
a_inter(8) 0 a_inter(9);
a_inter(5) a_inter(10) 0];
% CONVERT the parameters in MATRIX form for System 3

```

```

a_interaction3 = [0 a_inter(11) a_inter(2);
                  a_inter(12) 0 a_inter(13);
                  a_inter(5) a_inter(14) 0];
% NOTE that parameters a_inter(2) and a_inter(5) are common
% to all systems
%*****
% OPEN FILE "exp_tiel.txt" for Experimental data
fid = fopen('exp_tiel.txt','r');
% READ tie line data in (6,m) MATRIX
exptiel = fscanf(fid,'%g %g',[6 inf]);
% CLOSE "exp_tiel.txt"
fclose(fid);
% TAKE the transpose of MATRIX to make it (m,6)
exp_tiel = exptiel';
% INITIATE sum's
sum1=0;sum2=0;sum3=0;sum4=0;
% INITIATE v's
v1=0;v2=0;v3=0;v4=0;
% CALL "estimation1" for tie line estimation
% STORE them in a MATRIX
est_tiel = estimation1(m1,exp_tiel,a_interaction1);
% CALCULATE errors
error1 = exp_tiel - est_tiel;
% CALCULATE sum of errors
for i = 1:m1
    sum1= sum1+error1(i,1);
    sum2= sum2+error1(i,2);
    sum3= sum3+error1(i,4);
    sum4= sum4+error1(i,5);
end
% AVERAGE of errors
sum1 = sum1/m1; sum2 = sum2/m1; sum3 = sum3/m1;
sum4 = sum4/m1;
% ESTIMATE variances
for i = 1:m1
    v1 = v1+(error1(i,1)-sum1)^2;
    v2 = v2+(error1(i,2)-sum2)^2;
    v3 = v3+(error1(i,4)-sum3)^2;
    v4 = v4+(error1(i,5)-sum4)^2;
end
v1=v1/(m1-1);v2=v2/(m1-1);v3=v3/(m1-1);v4=v4/(m1-1);
% INITIATE
tem = 0;
% CALCULATE summation
for i=1:m1
    tem = tem + (error1(i,1))^2/v1+(error1(i,2))^2/v2+...
              (error1(i,4))^2/v3+(error1(i,5))^2/v4;

```

```

end

% CALCULATE the objective function
L1 = 2*m1*log(2*pi)+(m1/2)*log(v1*v2*v3*v4)+(1/2)*tem
p1 = L1;
sum_square = 0;
% CALCULATE the rmsd
for i=1:m1
    for j=1:6
        sum_square = sum_square+(est_tie1(i,j)-exp_tie1(i,j))^2;
    end
end
rms1 = 100*(sum_square/(6*m1))^0.5
%*****
% Instructions are similar as above
fid = fopen('exp_tie2.txt','r');
exptie2 = fscanf(fid,'%g %g',[6 inf]);
fclose(fid);
exp_tie2 = exptie2';
sum1=0;sum2=0;sum3=0;sum4=0;
v1=0;v2=0;v3=0;v4=0;
est_tie2 = estimation2(m2,exp_tie2,a_interaction2);
error2 = exp_tie2 - est_tie2;
for i = 1:m2
    sum1= sum1+error2(i,1);
    sum2= sum2+error2(i,2);
    sum3= sum3+error2(i,4);
    sum4= sum4+error2(i,5);
end
sum1 = sum1/m2; sum2 = sum2/m2; sum3 = sum3/m2;
sum4 = sum4/m2;
for i = 1:m2
    v1 = v1+(error2(i,1)-sum1)^2;
    v2 = v2+(error2(i,2)-sum2)^2;
    v3 = v3+(error2(i,4)-sum3)^2;
    v4 = v4+(error2(i,5)-sum4)^2;
end
v1=v1/(m2-1);v2=v2/(m2-1);v3=v3/(m2-1);v4=v4/(m2-1);
tem = 0;
for i=1:m2
    tem = tem + (error2(i,1))^2/v1+(error2(i,2))^2/v2...
               +(error2(i,4))^2/v3+(error2(i,5))^2/v4;
end
L2 = 2*m2*log(2*pi)+(m2/2)*log(v1*v2*v3*v4)+(1/2)*tem
p2 = L2;
sum_square = 0;
for i=1:m2

```

```

        for j=1:6
            sum_square = sum_square+(est_tie2(i,j)-
exp_tie2(i,j))^2;
        end
    end
    rms2 = 100*(sum_square/(6*m2))^0.5

%*****
fid = fopen('exp_tie3.txt','r')
exptie3 = fscanf(fid,'%g %g',[6 inf]);
fclose(fid);
exp_tie3 = exptie3';
sum1=0;sum2=0;sum3=0;sum4=0;
v1=0;v2=0;v3=0;v4=0;
est_tie3 = estimation3(m3,exp_tie3,a_interaction3);
error3 = exp_tie3 - est_tie3;
for i = 1:m3
    sum1= sum1+error3(i,1);
    sum2= sum2+error3(i,2);
    sum3= sum3+error3(i,4);
    sum4= sum4+error3(i,5);
end
sum1 = sum1/m3; sum2 = sum2/m3; sum3 = sum3/m3;
sum4 = sum4/m3;
for i = 1:m3
    v1 = v1+(error3(i,1)-sum1)^2;
    v2 = v2+(error3(i,2)-sum2)^2;
    v3 = v3+(error3(i,4)-sum3)^2;
    v4 = v4+(error3(i,5)-sum4)^2;
end
v1=v1/(m3-1);v2=v2/(m3-1);v3=v3/(m3-1);v4=v4/(m3-1);
tem = 0;
for i=1:m3
    tem = tem + (error3(i,1))^2/v1+(error3(i,2))^2/v2...
                +(error3(i,4))^2/v3+(error3(i,5))^2/v4;
end
L3 = 2*m3*log(2*pi)+(m3/2)*log(v1*v2*v3*v4)+(1/2)*tem
p3 = L3;
sum_square = 0;
for i=1:m3
    for j=1:6
        sum_square = sum_square+(est_tie3(i,j)-exp_tie3(i,j))^2;
    end
end

rms3 = 100*(sum_square/(6*m3))^0.5

```

```

%*****
% SUM all the objective funations
    L = L1+L2+L3

%*****
% FILE: estimation1.m
%*****
% FUNCTION DECLARE
function estimate = estimation1(m,exp_tie,a_interaction)
% Rk for three components
Rk = [4.4998 3.19051 4.0356];
% Qk for three components
Qk = [3.856 2.4 3.2 ];
% SPECIFY temperature
temp =298.15;
for i=1:m
% ESTIMATE mid point of tie lines
    z_1 = (exp_tie(i,1)+exp_tie(i,4))/2;
    z_2 = (exp_tie(i,2)+exp_tie(i,5))/2;

% initial guess of a tie line
    X0 = exp_tie(i,:);
% CALL "lle_equation" for setting LLE equations
% CALL "fosolve" for Solving equations
X = fsolve('lle_equation',X0,[],[],z_1,z_2,Rk,Qk,
    a_interaction, temp);
% STORE the tie lines in a MATRIX
    for j=1:6
        est(i,j) = X(j);
    end
    estimate = est;
end

%*****
% FILE: estimation2.m
%*****
% INSTRUCTION are similar to estimation1
function estimate = estimation2(m,exp_tie,a_interaction)
Rk = [4.4998 3.92287 4.0356];
Qk = [3.856 2.968 3.2 ];
temp =298.15;
for i=1:m
    z_1 = (exp_tie(i,1)+exp_tie(i,4))/2;
    z_2 = (exp_tie(i,2)+exp_tie(i,5))/2;
    X0 = exp_tie(i,:);

```

```

X = fsolve('lle_equation',X0,[],[],z_1,z_2,Rk,Qk,
          a_interaction,temp);

double(X);
for j=1:6
    est(i,j) = X(j);
end
estimate = est;
end

%*****
% FILE: estimation3.m
%*****
% INSTRUCTION are similar to estimation1
function estimate = estimation3(m,exp_tie,a_interaction)
Rk = [4.4998 4.65788 4.0356];
Qk = [3.856 3.536 3.2 ];
temp =298.15;
for i=1:m

    z_1 = (exp_tie(i,1)+exp_tie(i,4))/2;
    z_2 = (exp_tie(i,2)+exp_tie(i,5))/2;
    X0 = exp_tie(i,:);
    X = fsolve('lle_equation',X0,[],[],z_1,z_2,Rk,Qk,
              a_interaction,temp);

    double(X);
    for j=1:6
        est(i,j) = X(j);
    end
    estimate = est';
end

```

## A.4 Program to estimate temperature dependent parameters

```
%*****
% FILE: initial_temp.m
% INCLUDE objective_temp.m
% INCLUDE estimation_temp.m
% INCLUDE lle_equation.m           % same as above
% INCLUDE uniquac.m               % same as above
% INCLUDE unifac.m                % same as above
% INCLUDE nrtl.m                  % same as above
% INCLUDE exptie.txt              % It will contain
                                   temperature also
%*****

global LK;
global rms;
global itr;
% START iteration
itr = 0;
% number of function evaluation
options(14) = 5000;
% INITIAL guess of parameters
% a_inter0 = [a(1,2) a(1,3) b(1,2) b(1,3)..
              a(2,1) a(2,3) b(2,1) b(2,3)..
              a(3,1) a(3,2) b(3,1) b(3,2)];
a_inter0 = [1083.86 -10.82902 246.3237 -2.25353 -1.1681 -
11.3614 1.245044 -2.804212];
% CALL FILE: "activity_temp" for objective function
% CALL "fmins" for minimization
a_inter = fmins('activity_temp',a_inter0,options)
% OPEN FILE "out.txt" for output
fiid = fopen('out.txt','a');
% PRINT initial guess
fprintf(fiid,'initial guess = %g %g %g %g %g %g %g %g %g %g %g\n',a_inter0);
% PRINT parameters
fprintf(fiid,'parameters = %g %g %g %g %g %g %g %g %g %g %g\n',a_inter);
% PRINT objective functions
fprintf(fiid,'L = %g %g %g\n',LK);
% PRINT rmsd's
fprintf(fiid,'pl = %g %g %g\n',rms);
% PRINT no of iterations
fprintf(fiid,'iterations = %d',itr);
% CLOSE FILE "out.txt"
fclose(fiid);
```

```

%*****
% FILE: objective_temp.m
%*****
function ob_fun = errorsq(a_inter)
global LK;
global rms;
global itr;
% SPECIFY number of tie lines for each system
no_tie = [7,7,6];
no_tieline = no_tie;
% SPECIFY number of temperatures for which data are
no_data = 3;
itr = itr+1
% STORE the parameters in MATRIX form
% a_interaction = [0 a(1,2)a(1,3)0 b(1,2)b(1,3);
%                 a(2,1) 0 a(2,3)b(2,1)0 b(2,3);
%                 a(3,1)a(3,2) 0 b(3,1)b(3,2)0 ];
a_interaction=[0 a_inter(1)a_inter(2)0 a_inter(3)a_inter(4;
               a_inter(5)0 a_inter(6) a_inter(7) 0 a_inter(8);
               a_inter(9)a_inter(10)0a_inter(11)a_inter(12) 0]
% OPEN FILE "exptie.txt"
fid = fopen('exptie.txt','r');
% READ data in a MATRIX of (7,m)
exptie = fscanf(fid,'%g %g',[7 inf]);
% CLOSE FILE "out.txt"
fclose(fid);
% TRANSPOSE the MATRIX to make it (m,7)
exp_tie = exptie';

% CALCULATE total number of tie lines
term = 0;
for k=1:no_data
    term = term + no_tie(k);
    no_tie(k) = term;
end
% CALL "estimation_temp" for tie line estimation
est_tie=estimation(a_interaction,exp_tie,no_tie(no_data));
% STORE experimental tie line data in MATRIX
exp_tie = exp_tie(:,1:6);
% ESTIMATE the errors
error = exp_tie - est_tie;
no_tie;
term1 = 0;
term2 = 0;
term3 = 0;
objective = 0;

```

```

% ESTIMATE all objective functions for all temperature data
for k = 1:no_data
    sum_square(k) = 0;
    sum1=0;sum2=0;sum3=0;sum4=0;
    v1=0;v2=0;v3=0;v4=0;
    m = no_tieline(k);
    for i = term1+1:no_tie(k)
        term1 = no_tie(k);
        sum1= sum1+error(i,1);
        sum2= sum2+error(i,2);
        sum3= sum3+error(i,4);
        sum4= sum4+error(i,5);
    end
    sum1 = sum1/m; sum2 = sum2/m;
    sum3 = sum3/m; sum4 = sum4/m;
    for i = term2+1:no_tie(k)
        term2=no_tie(k);
        v1 = v1+(error(i,1)-sum1)^2;
        v2 = v2+(error(i,2)-sum2)^2;
        v3 = v3+(error(i,4)-sum3)^2;
        v4 = v4+(error(i,5)-sum4)^2;
    end
    v1=v1/(m-1);v2=v2/(m-1);v3=v3/(m-1);v4=v4/(m-1);
    tem = 0;
    for i=term3+1:no_tie(k)
        term3=no_tie(k);
        tem = tem +(error(i,1))^2/v1+(error(i,2))^2/v2+
            (error(i,4))^2/v3 + (error(i,5))^2/v4;
        for j = 1:6
            sum_square(k) = sum_square(k)+(error(i,j))^2;
        end
    end

    end
    L(k) = 2*m*log(2*pi)+(m/2)*log(v1*v2*v3*v4)+(1/2)*tem;
    objective = objective + L(k);
    rmsd(k) = 100*(sum_square(k)/(m*6))^0.5;
    LK(k) = L(k);
    rms(k)=rmsd(k);
end
L
% ob_fun is sum of all objective functions
ob_fun = objective
rmsd

```

```

%*****
% FILE: estimaton_temp.m
%*****
function estimate = estimation(a_interaction,exp_tie,m)
for i=1:m
    z_1 = (exp_tie(i,1)+exp_tie(i,4))/2;
    z_2 = (exp_tie(i,2)+exp_tie(i,5))/2;
    X0 = exp_tie(i,1:6);
    temp = exp_tie(i,7);
    X = fsolve('fun',X0,[],[],z_1,z_2,a_interaction,temp);
double(X);
for j=1:6
    est(i,j) = X(j);
end
estimate = est;
end

```